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Abstract: Water retention curve (WRC) is an important tool to study the hydraulic and mechanical properties of unsaturated soils, such as permeability, strength and deformation properties. Most of the existing WRC models fail to reflect the water retention mechanisms of unsaturated soils or they are complex in form, and these models are hard to give good performance on modelling the bimodal and multimodal WRCs. In this study, based on analyzing the water retention mechanisms of unsaturated soils, the WRC was divided into two domains that are governed by adsorption and capillary mechanisms, respectively. An adsorption water retention curve model (WRCM) was developed based on micro-pore filling theory and Kelvin's law. A capillary WRCM was established based on the capillary condensation theory and Young-Laplace equation. Then, a new water retention curve model over the full suction range was built by superposing the adsorption and capillary WRCMs. Finally, the new model was validated through modelling the experimentally measured WRCs of six representative unsaturated soils, including Shanghai soft clay, Xi'an loess, Nanyang expansive soil, Guilin lateritic clay, Western Liaoning aeolian soil and Inner Mongolia Gaomiaozi (GMZ) bentonite. Results showed that the proposed model, which was simple in form with definite physical meaning parameters and successfully reflected the adsorption and capillary mechanisms of water retention, was able to simulate WRCs with different shapes for different types of soils under different conditions.

Keywords: unsaturated soils; water retention curve (WRC); micro-pore filling; capillary condensation; water retention model

1 Introduction

In engineering practice, soils are mostly in unsaturated condition. When the air relative humidity (or suction) changes, the water retention capacity (water content or saturation) of unsaturated soils will change accordingly. The water retention curve (WRC or SWRC) or the soil-water characteristic curve (SWCC) can characterize the relationship between suction and water retaining capacity in unsaturated soils^[1]. The WRC can be used to predict the hydraulic–mechanical properties of unsaturated soils such as permeability, strength and deformation properties. It is an important tool for studying the properties of unsaturated soils^[2–4].

The WRC can be obtained by two ways, including measuring the water content when controlling the relative humidity (or suction) and measuring the relative humidity (or suction) when controlling the water content. The former method can be achieved using methods such as axial translation method, vapor phase technique and osmotic method, and the latter one mainly involves measuring the suction of specimens with different water contents using suction

measuring devices (psychrometer, tensiometer, dew-point water potential meter)^[5]. However, these test methods are usually demanding and time consuming. Only a small number of discrete data points can be obtained, which makes it difficult to obtain a complete WRC over the full suction range. Especially for low permeability soils such as compacted bentonite, it can take weeks or even longer to determine just one data point^[6]. Therefore, the WRC over the full suction range usually needs to be obtained indirectly with the help of mathematical models or to be predicted from other WRC under different conditions based on fitting parameters. The mathematical model describing the WRC is called the water retention curve model (WRCM).

Many scholars have developed many different types of WRCMs for unsaturated soils, including: (i) empirical or semi-empirical WRCMs based on curve shape or statistical analysis, such as the traditional BC model, VG model and FX model^[7–9]; (ii) WRCMs that involve particle size distribution or pore structure characteristics^[10–13]; (iii) WRCMs that use soil deformation^[14–15]; (iv) WRCMs based on basic theories such as thermodynamics, fractal

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theory or surface science^[16–18], and (v) WRCMs that consider adsorption and capillary water retention mechanisms^[19–20]. All these models can properly describe the WRCs under specific conditions and have played an important role in the study of coupled constitutive models for unsaturated soils.

However, the water retention behaviour of unsaturated soils are influenced by many factors such as their mineral composition, dry density (void ratio), pore structure (size, distribution and connectivity of pore), deformation behaviour, stress history and temperature^[21–22]. Therefore, there are different forms of WRCs (single, double or multiple peaks), which are difficult to be described by the traditional unique-expression WRCMs. Qi et al^[23] deduced a all-purpose WRCM expressed by a power function polynomial on the basis of analyzing 4 types of representative WRCMs. This model can simulate various shapes of WRCs, and its simulation accuracy can be improved by increasing the number of polynomial terms. However, the physical meanings of the model parameters are unclear.

In this paper, based on the water retention mechanism of unsaturated soils, the WRCs were divided into two parts, namely adsorption water retention domain and capillary water retention domain. An adsorption WRCM was constructed based on the micro-pore filling theory. A capillary WRCM was constructed based on the capillary condensation theory. A new WRCM of unsaturated soils over the full suction range was then established. Finally, the model was validated using experimentally measured WRCs of six representative soils, and the applicability and limitations of the new model were discussed. Compared with the existing models, the model in this paper has simpler expressions and clearer physical meanings of the parameters and can simulate the WRCs of different types of unsaturated soils.

2 Water occurrence and water retention mechanisms

Unsaturated soil is a porous medium with two phases of gas and solid or three phases of gas, liquid and solid. The pore water includes adsorbed water, capillary water, and gravitational water. Gravitational water is mainly present in the large pores when the suction is low, and its content is small and difficult to be reflected in the WRC obtained from the experimental tests. Therefore, the gravitational water is not involved in this paper. There is an example about clay to explain pore water in unsaturated soil. As the environmental suction decreases, water molecules will be drawn into the interlayer pores with the lowest matrix potential energy and combined with the interlayer cations to form interlayer adsorbed water;

then the interlayer adsorbed water will be attracted by the particle surface cations and electrostatic forces to form the surface adsorbed water (i.e. bound water film). As the environmental suction further reduces, more water molecules condense on the particle surface, and interact with the particle surface and the air to produce a mechanically balanced meniscus water column. Finally, interparticle capillary water will be formed (Fig.1)^[24–25].

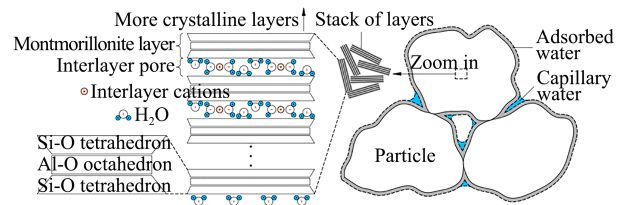


Fig. 1 Adsorbed water and capillary water in unsaturated clay

The above analysis shows that the main water retention mechanisms of unsaturated soils are adsorption and capillary effects in the high and low suction ranges. It has been shown that the adsorbed water content is mainly related to the properties of the gas–liquid–solid interface (cation exchange capacity, specific surface area); Although the capillary water content is also related to the properties of the gas–liquid–solid interface (e.g. surface tension, contact angle), it is mainly related to the pore structure characteristics (size, distribution, connectivity of pore)^[26]. Factors such as mineral composition, temperature and chemistry in pore water essentially influence the gas–liquid–solid interface properties. Factors such as dry density, stress history and boundary conditions essentially influence the pore structure characteristics. Thus, these factors will affect the water retention behaviour of unsaturated soils. The WRCs of the same type of soil almost coincide in the high suction range. In the low suction range, they are affected by the factors such as dry density, temperature, and boundary conditions^[27–28]. Adsorbed water and capillary water have different effects on the strength, permeability and volumetric deformation characteristics of unsaturated soil. However, most of traditional unsaturated soil mechanics theories only consider capillary water or do not distinguish between them. These result in difference between calculated and measured results. Quantitative differentiation between adsorbed water and capillary water is of great guiding significance for engineering design, construction and safety evaluation in water retaining and drainage of soil, deformation prediction, bearing capacity calculation.

3 Modelling the water retention curve

Based on the above analysis, the WRCs of unsaturated

soils can be divided into two parts: the adsorption and capillary WRCs (Fig.2). The adsorption and capillary WRCs can be modelled separately to establish a WRCM for unsaturated soils in the full suction range. In this conceptual model, the WRC is formed by superimposing the adsorption and capillary WRCs. The adsorption WRC starts at the highest suction and gradually increases and stabilises as the suction decreases. The capillary WRC starts at a lower suction and gradually increases and stabilises as the suction decreases.

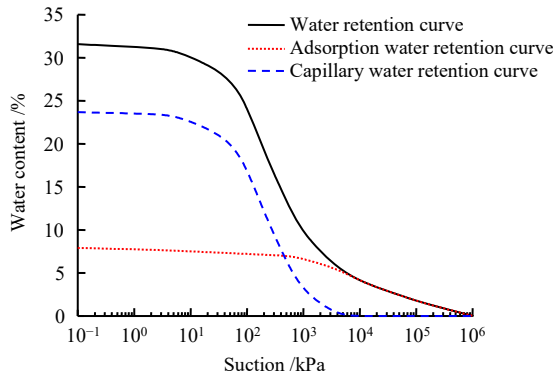


Fig. 2 Conceptual model of water retention for unsaturated soils

3.1 Adsorption water retention curve model

In the field of colloid and interfacial chemistry, the curve of adsorption versus gas equilibrium relative pressure at a constant temperature is known as the adsorption isotherm^[29]. By definition, in fact the WRC for unsaturated soils is also a generalized adsorption isotherm. Therefore, an adsorption WRCM can be considered from the adsorption isotherm model.

Many scholars have proposed adsorption isotherm models, for example, the popular Langmuir monolayer adsorption model, the Freundlich multilayer adsorption model, the BET multilayer adsorption model, the FHH adsorption model and the D-R micro-pore filling theory model. These models are applicable to adsorbent materials with different pore characteristics^[29]. For unsaturated soils with multiple pore structure characteristics, water vapour adsorption mainly occurs in the interlayer pores and inter-stack pores. The interlayer pores are of molecular scale size and are suitable to be described by the micro-pore filling theory model. The inter-stack pores are slightly larger in size and can gradually form diffused double electric layer and are suitable to be described by the multi-molecular layer adsorption model. However, modelling the inter-layer pores and the inter-stack pores separately would make the final model expressions for the WRC very complex. Therefore, in this paper, appropriate modifications to the micro-pore filling theory model are considered so that it can be applied to describe the adsorption

WRCs of unsaturated soils.

The micro-pore filling theory was established based on the adsorption potential theory. The concept of adsorption potential was first introduced by Eucken (1914) and the adsorption potential theory was established by Polanyi (1914)^[30]. The adsorption potential is defined as the change in Gibbs' free energy per unit mole resulting from moving 1 mol of an ideal gas from an infinite distance (i.e. outside the adsorption space unaffected by adsorption forces) to a point in the adsorption layer at constant temperature, shown as following:

$$\varepsilon = -\Delta G = \int_p^{p_0} V dp = RT \ln(p_0 / p) \quad (1)$$

where ε is the adsorption potential; ΔG is the increment of Gibbs free energy; p is the equilibrium pressure of the gas; p_0 is the saturation vapour pressure of the gas (constant at constant temperature); and V is the molar volume of the gas. It can be seen from Eq.(1) that the adsorption potential ε decreases and the adsorption of the interface to water vapour molecules decreases as the equilibrium pressure p increases (i.e. the relative humidity increases).

Influenced by the Van der Waals potential of the pore wall, adsorption does not occur layer by layer on the pore wall, but by volume filling within the micro-pore. Dubinin et al^[31] proposed the well-known D-R micro-pore filling model based on the Polanyi adsorption potential theory. It is assumed that the pore size distribution obeys the Gauss function:

$$V_a = V'_0 \exp(-\eta \varepsilon^2) \quad (2)$$

where V_a is the volume of adsorbate at an adsorption potential of ε ; V'_0 is the micro-pore volume; and η is a constant.

However, the assumptions of the D-R model are too idealistic. It is therefore only applicable to micro-pore porous media with a uniform and narrow distribution of pore sizes. Dubinin et al^[32] proposed the D-A model by slightly improving the D-R model:

$$V_a = V_0 \exp[-(\varepsilon / E)^m] \quad (3)$$

where E is the characteristic energy of adsorption; m is a constant; and V_0 is the volume of pore holding the adsorbed water (pore may also retain capillary water meanwhile). The D-A model has been proved to successfully describe the adsorption WRCs of unsaturated soils such as compacted bentonites with multiple pore characteristics^[20].

Substituting Eq.(1) into Eq.(3) and then combining it with Kelvin's law, we can organize it to obtain:

$$V_a = V_0 \exp[-(\beta \psi_a)^m] \quad (4)$$

where $\beta = M_w / \rho_w E$, M_w is the molar mass of water molecules; ρ_w is the water density; and ψ_a is the adsorption suction.

When suction is 0, there should be $V_a < V_0$ due to the capillary water occupying a certain pore volume. Therefore, Eq.(4) was amended as follows:

$$V_a = \alpha V_0 \exp[-(\beta \psi_a)^m] \quad (5)$$

where α is a coefficient, $0 < \alpha < 1$.

Based on the definition of volumetric water content, Eq.(5) can be further rewritten as

$$\theta_a = \theta_{a\max} \exp[-(\beta \psi_a)^m] \quad (6)$$

where θ_a is the adsorbed volumetric water content; $\theta_{a\max}$ is the maximum adsorbed volumetric water content, $\theta_{a\max} = \alpha V_0 / V$, V is the total volume of the sample.

Equation (6) shows that the adsorption volumetric water content will be only equal to 0 when the suction tends to infinity, which is clearly unrealistic. In fact, when the suction rises up to levels of 300–1 200 MPa (depending on the mineral composition), the soil sample reaches a completely dry state^[33]. Therefore, Eq.(6) was further refined as

$$\theta_a = \theta_{a\max} [1 - \exp(1 - \psi_{a\max} / \psi_a)^m] \quad (7)$$

where $\psi_{a\max}$ is the maximum adsorption suction. When the adsorption suction $\psi_a = \psi_{a\max}$, $\psi_a = 0$; and when the suction $\psi_a = 0$, $\theta_a = \theta_{a\max}$. Thereby Eq.(7) is the adsorption WRM. The model is based on the D-R model for micro-pores. However, due to the improvement of the D-R model by introducing the characteristic energy of adsorption E and the parameter m (Eq.(3)), it is applicable to describe the adsorption WRCs of unsaturated soils with various pore characteristics.

3.2 Capillary water retention curve model

With the decrease of suction, capillary condensation begins to appear in the pores. When the suction reaches equilibrium, the pore pressure, water pressure and surface tension are all in an equilibrium state, thus the Young-Laplace equation can be easy to be derived:

$$d = \frac{4T_s}{\psi_c} \cos \gamma \quad (8)$$

where d is the pore diameter; T_s is the surface tension of water; γ is the contact angle of water on the particles surface; and ψ_c is the capillary suction.

Equation (8) shows that pores with a pore size less than d will be saturated for a given capillary suction (Fig.3). The capillary water retention is therefore related to the pore size distribution. Influenced by the factors such as dry density, water content and boundary conditions, the

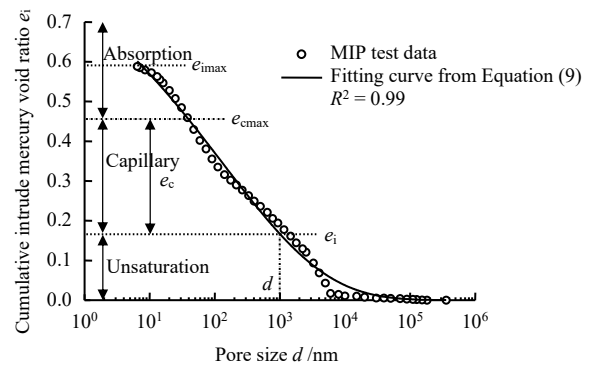


Fig.3 Relationship between capillary void ratio and cumulative mercury-intruded void ratio

pore size distribution curve of unsaturated soils may exhibit single, double or even multiple peaks and cannot be described by a unique mathematical model. However, its cumulative mercury-intruded volume always increases with decreasing $\lg d$ (Fig.3). For simplicity, it is assumed that the cumulative mercury-intruded void ratio (the ratio of cumulative mercury-intruded volume to soil particle volume) can be roughly expressed as

$$e_i = e_{i\max} \exp(-bd^n) \quad (9)$$

where $e_{i\max}$ is the maximum cumulative mercury-injected void ratio; b and n are fitting parameters. The cumulative mercury-intruded void ratio of the Gaomiaozi bentonite with dry density of 1.45 g/cm³ and suction of 113 MPa, for example, can be properly fitted by Eq.(9) (Fig.3).

Based on the implications of the Young-Laplace equation, when the suction is ψ_c , the cumulative void ratio e_c occupied by capillary water (hereafter referred to as the capillary void ratio) is written as

$$e_c = e_{c\max} - e_i = e_{c\max} [1 - \lambda \exp(-bd^n)] \quad (10)$$

where $e_{c\max}$ is the maximum value of the capillary void ratio, $\lambda = e_{i\max} / e_{c\max} > 1$.

Substituting Eq.(8) into Eq.(10) gives

$$e_c = e_{c\max} [1 - \lambda \exp(-k / \psi_c^n)] \quad (11)$$

where $k = b(4T_s \cos \gamma)^n$.

In terms of the definition of volumetric water content, Eq.(11) can be further rewritten as

$$\theta_c = \theta_{c\max} [1 - \lambda \exp(-k / \psi_c^n)] \quad (12)$$

where θ_c is the capillary volumetric water content; $\theta_{c\max}$ is the maximum capillary volumetric water content, $\theta_{c\max} = e_{c\max} (1 - e_{\text{total}})$, and e_{total} is the total void ratio. Equation (12) is the capillary WRCM.

3.3 Water retention curve model for unsaturated soils

Based on the concept shown in Fig.2, the WRCM

for the full suction range can be obtained by superimposing Eqs. (7) and (12) as follows:

$$\theta = \theta_{a\max} [1 - \exp(1 - \psi_{\max} / \psi)^m] + \theta_{c\max} [1 - \lambda \exp(-k / \psi^n)] \quad (13)$$

where $\psi = \psi_a + \psi_c$. Since the main water retention mechanisms in the high and low suction ranges are adsorption and capillary effects, respectively, $\psi_{\max} = \psi_{a\max}$, in the first term $\psi \approx \psi_a$, and $\psi \approx \psi_c$ in the second term on the right-hand side of the equation. Based on the determination of the model parameters, the adsorbed and capillary water contents for specific suction can be quantified by Eq.(13). This provides a basis for improving the theory of strength, permeability, and deformation in unsaturated soils.

Based on the proportion relationship of the three phases of the soil, Eq.(13) can also be converted into a WRCM expressed by mass water content w and degree of saturation S_r .

4 Model validation

To verify the applicability of the model proposed in this paper, the experimentally measured WRCs of six common representative soils, including Shanghai soft soil^[34], Xi'an loess^[35], Nanyang swelling soil^[36], Guilin red clay^[37], Liaoxi aeolian soil^[38] and Inner Mongolia Gaomiaozi (GMZ) bentonite^[39–40], were simulated using the model in this paper (Eq.(13)), the VG model^[8] and the FX model^[9]. The results of the simulations are shown in Fig.4. As can be seen from the figure, the fitted results

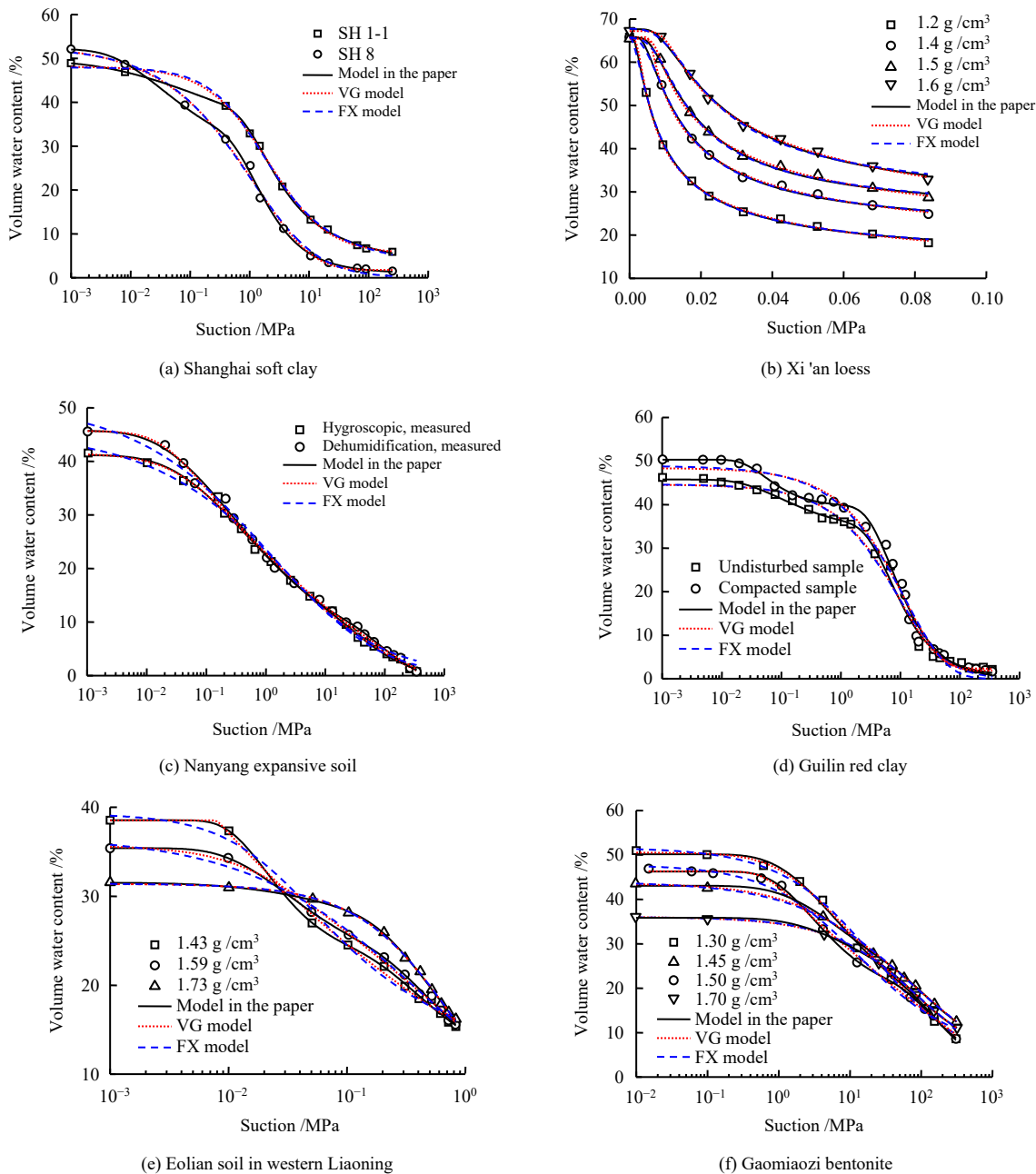


Fig. 4 Comparison of the measured and simulated water retention curves

agree well with the experimentally measured results for different shapes of WRCs for different types of soils under different conditions (the R^2 of all fitting curves is greater than 0.996). This indicates that the model in this paper can simulate the WRCs of common unsaturated soils very well. Especially for the WRC of Guilin red clay (Fig.4(d)), the traditional VG model^[8] and FX model^[9] cannot accurately depict its bimodal shape characteristics. However, the fitted results of model in this paper almost perfectly agree with the experimentally measured results.

5 Discussion

5.1 Meanings of model parameters and differences in fitting parameters

The model in this paper (Eq.(13)) has seven parameters, where parameters $\theta_{a\max}$ and $\theta_{c\max}$ are the maximum adsorption volumetric water content and maximum capillary volumetric water content. Parameter ψ_{\max} is the maximum suction. Parameter λ is related to the pore size distribution (Eq.(10)). Parameter k is related to the pore size distribution, capillary water surface tension and contact angle (Eq.(11)). Parameters m and n are fitting parameters. Except for parameters m and n , the other five parameters have clear physical meanings.

Table 1 presents the fitting values of the model parameters for the experimentally measured WRCs of the six representative soils (Fig.4). By comparing the data in the table, it can be seen that a high clay mineral content leads to a large ψ_{\max} . This correctly reflects the rule that the water retention capacity increases with increasing clay mineral content. In addition, the parameter m varies less with specimen conditions for the same soil, whereas parameters k and n vary more with specimen conditions. This can be explained that the former parameter is mainly related to the factors such as mineral composition and specific surface area, while the latter parameters are related to the pore size distribution. However, the model parameters do not vary clearly with the dry density of the specimen and other factors. Some of the fitting values of the parameters are even unreasonable. For example, the fitting values for soft clay, red clay, aeolian soil and bentonite are all less than 1, which is not consistent with the definition of $\lambda > 1$ (Eq.(10)). For another instance, the $\theta_{a\max}$ of Nanyang swelling clay and Gaomiaozi bentonite are clearly smaller than those of other soils with less clay minerals. This may be due to the facts that: (i) A reasonable range of values for each parameter was not set during the fitting calculations, and the principle was only to achieve the best fit; (ii) The deformation behaviour and the boundary conditions of the water retention tests for various soils were different (except for the Gaomiaozi

bentonite which has the constant volume, the other soils were all free swelling), which results in difference between change laws of different pore structures; (iii) Even for the same soil (e.g. Liaoxi aeolian soil), the shape of the WRC varies considerably under different conditions. Although the different WRCs can be fitted well based on these fitting parameters (Fig.4), it is likely that unreasonable adsorption and capillary WRCs will be obtained. This will prevent the correct prediction of the adsorbed and capillary water contents for a given suction. Therefore, a reasonable value range for each parameter of the model should be set separately according to the meaning of the parameter.

Table 1 Fitted values of model parameters

Material	Number / Conditions	$\theta_{a\max}$	ψ_{\max}	m	$\theta_{c\max}$	λ	k	n
Soft clay	SH 1-1	22.72	240.83	0.008	26.766	0.974	0.753	0.233
	SH 8	25.41	117.57	0.011	26.671	0.955	0.190	0.497
	1.2 g/cm ³	29.14	111.05	0.682	36.700	1.438	0.014	0.854
Loess	1.4 g/cm ³	31.32	97.34	0.802	34.490	1.317	0.008	1.088
	1.5 g/cm ³	31.19	98.16	0.315	34.400	1.195	0.007	1.202
	1.6 g/cm ³	33.03	108.76	0.296	34.570	1.211	0.012	1.167
Expansive clay	Hygroscopic	3.56	644.14	0.062	37.580	1.081	0.777	0.342
	Dehumidification	5.25	889.19	0.109	40.460	1.078	0.635	0.356
Red clay	Undisturbed	31.88	170.07	0.040	13.860	0.859	0.241	0.615
	Compacted	37.73	164.91	0.044	12.570	0.860	0.044	1.070
Aeolian soil	1.43 g/cm ³	12.38	44.56	0.010	26.170	0.604	0.007	1.299
	1.59 g/cm ³	12.71	51.08	0.011	22.690	0.633	0.063	0.802
	1.73 g/cm ³	13.17	50.05	0.010	18.360	1.743	1.301	0.256
	1.30 g/cm ³	11.40	2 802.50	0.073	38.760	1.053	2.649	0.515
Bentonite	1.45 g/cm ³	14.78	1 901.10	0.079	31.480	0.909	2.239	0.731
	1.50 g/cm ³	8.23	2 199.10	0.065	34.820	0.883	2.870	0.458
	1.70 g/cm ³	8.69	2 184.40	0.041	27.150	0.914	3.471	0.410

5.2 Limitations of the model

The model mechanism in this paper is clear and simple and is able to fit WRCs well for various types of soils and shapes. However, there are still some shortcomings that need to be improved.

(1) The capillary water retention model (Eq.(12)) does not limit the maximum suction ψ_{\max} . This may result in the capillary water content only tends to 0 when the suction approaches infinity in some fitting curves. This may also cause capillary water only to exist in the very high suction, which do not agree with the actual situation obviously.

(2) Both the adsorption water retention model (Eq. (7)) and the capillary water retention model (Eq.(12)) are convex functions that increase monotonically with decreasing suction. This means that the combination of these two has at most two peaks. Therefore, the model in this paper (Eq.(13)) can only simulate WRCs with single or double peaks but cannot accurately simulate WRCs with three or more peaks. However, most of the WRCs

of common unsaturated soils in engineering are single-peaked or double-peaked, thus the WRCs can be simulated using the model proposed in this paper.

Based on the principle of making the model mechanism as clear and simple as possible, improvements to the model can be considered in terms of limiting the maximum capillary suction, improving the assumption of capillary void ratio, and revising the micro-pore filling theory.

6 Conclusions

Based on the water retention mechanism of unsaturated soils, two WRCMs were constructed in this paper, including the adsorption WRCM based on the micro-pore filling theory and the capillary WRCM based on the capillary condensation theory. From these, the WRCMs for unsaturated soils in the full suction range are established. The following conclusions are obtained:

(1) In the high and low suction ranges, the main water retention mechanisms of unsaturated soils are adsorption and capillarity, respectively. Adsorption is mainly related to properties of the gas–liquid–solid interface (cation exchange capacity, specific surface area). Capillarity is mainly related to the structural characteristics of the pores (size, distribution, connectivity of pore).

(2) Based on the micro-pore filling theory and combined with Kelvin's law, an adsorption WRCM was constructed (Eq.(7)), which contains three parameters.

(3) Based on the capillary condensation theory and combined with the Young-Laplace equation, an adsorption WRCM (Eq.(12)) was constructed, which contains four parameters.

(4) The WRCs of unsaturated soils in the full suction range are established by superimposing the adsorption and capillary WRCMs. This model has a simple form, and the parameters have clear physical meanings. It can reflect the water retention mechanism of unsaturated soils by adsorption and capillary effects and can be applied to simulating different shapes of WRCs for different types of unsaturated soils under different conditions.

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