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A Diffusion-Controlled Model for Swelling Behavior in Polymeric Hydrogels

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ABSTRACT

Hydrogels are cross-linked polymer networks capable of absorbing large amounts of water, supporting diverse biomedical, pharmaceutical, and agricultural applications. Their swelling behavior is governed by water diffusion within the polymer matrix and is commonly described by the classical Crank solution for Fickian diffusion in a plane sheet, expressed in terms of the normalized fractional water uptake (*Mt/M∞).* Therefore, an additional conversion is required to relate it to the swelling degree *S(t).*This study presents the one-dimensional Fickian diffusion solution for a hydrogel slab of thickness L, with surfaces held at a constant equilibrium concentration, and recasts it as a closed-form expression for the time-dependent swelling degree, *S(t)*, directly in terms of the effective diffusion coefficient *(D)* and the equilibrium swelling degree (S_{eq}). The resulting solution reproduces characteristic Fickian relationship $S(t) \propto t^{1/2}$at short times, and predicts the scaling law $t_{90} \propto L^2/D$. Parametric analysis further shows that D/L^2governs the swelling rate, whereas S_{eq} determines the equilibrium swelling capacity. The predicted trends are qualitatively consistent with reported hydrogel swelling behavior. Whereas the classical Crank model focuses on relative water uptake, the proposed formulation translates diffusion kinetics into the swelling degree, *S(t)*, enabling direct interpretation of measurable swelling behavior through a simple and physically meaningful analytical framework.

Keywords: Diffusion Coefficient, Fickian Diffusion, Hydrogel, Swelling Degree

ABSTRAK

Hidrogel merupakan jaringan polimer berikatan silang yang mampu menyerap air sehingga banyak dimanfaatkan dalam bidang biomedis, farmasi, dan pertanian. Perilaku pembengkakan hidrogel dipengaruhi oleh difusi air di dalam matriks polimer dan umumnya dijelaskan melalui solusi klasik Crank untuk difusi Fick pada lembaran datar, yang dinyatakan dalam bentuk fraksi penyerapan air ternormalisasi (*Mt/M∞*). Sehingga hal tersebut memerlukan langkah konversi tambahan sebelum dapat dibandingkan dengan derajat pengembangan *S(t).* Penelitian ini menyajikan solusi difusi Fick satu dimensi untuk lempeng hidrogel dengan ketebalan L yang kedua permukaannya dijaga pada konsentrasi kesetimbangan konstan, dan menyatakannya secara langsung sebagai ekspresi tertutup untuk *S(t)* dalam koefisien difusi efektif (D) dan derajat pengembangan kesetimbangan (S_{eq}), Solusi yang diperoleh menghasilkan hubungan karakteristik difusi Fick, yaitu $S(t) \propto t^{1/2}$ pada waktu awal, serta memprediksi hubungan $t_{90} \propto L^2/D$. Analisis parametrik menunjukkan bahwa D/L^2 mengendalikan laju pembengkakan, sedangkan S_{eq} menentukan kapasitas pembengkakan pada kondisi kesetimbangan. Hasil yang diperoleh secara kualitatif sesuai dengan perilaku pengembangan hidrogel yang dilaporkan dalam literatur. Berbeda dari model

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Crank yang berfokus pada serapan air relatif, formulasi yang diusulkan pada penelitian ini menerjemahkan kinetika difusi ke dalam derajat pengembangan, *S(t)*, sehingga memungkinkan interpretasi langsung terhadap perilaku pengembangan yang terukur melalui kerangka analitik yang sederhana dan bermakna secara fisik.

Kata kunci: Derajat Pengembangan, Difusi Fick, Hidrogel, Koefisien Difusi

1. Introduction

Hydrogels are three-dimensional (3D) cross-linked hydrophilic polymer networks capable of absorbing and retaining large amounts of water or biological fluids while preserving their structural integrity [1]. Their unique combination of high water content, excellent biocompatibility, tunable mechanical properties, and structural flexibility enables them to replicate the physicochemical characteristics of natural soft tissues. These features have attracted considerable attention and promoted the widespread use of hydrogels in diverse fields, including controlled drug delivery systems [2], tissue engineering and regenerative medicine [3], wound dressing materials [4], biosensing platforms [5], and agricultural superabsorbents for improving water retention and nutrient management in soil [6].

The fundamental property that defines the performance of hydrogels in these applications is their swelling behavior, commonly quantified by the swelling degree (*SD*), defined as the ratio of the absorbed water mass to the dry mass of the polymer network [7]. Mathematically, hydrogel swelling kinetics are commonly described by Fickian diffusion theory, where solvent transport follows Fick's second law of diffusion provided that diffusion is significantly slower than polymer-chain relaxation [8], [9]. Under these conditions, the effective diffusion coefficient can be considered approximately constant, and the swelling kinetics are governed primarily by solvent transport rather than polymer relaxation.

For a planar hydrogel with thickness L, the water concentration profile, *c(z,t)*, is governed by a partial differential equation that, under appropriate initial and boundary conditions, provides the time-dependent fractional water uptake, *Mt/M∞* [10]. This framework has been successfully applied to various hydrogel systems, including polyacrylamide–cellulose nanocrystal hydrogels, where the swelling kinetics were experimentally shown to follow a Fickian diffusion mechanism, as well as pH-responsive hydrogel membranes and other water-swollen polymer networks [11]–[14].

Despite the fundamental role of diffusion-controlled transport in hydrogel swelling, most analytical models for conventional non-reactive hydrogels are formulated in terms of the normalized fractional water uptake, M_t/M_∞, based on the classical Fickian diffusion framework. Although these formulations provide an accurate description of solvent diffusion, they do not directly express the swelling degree commonly measured in gravimetric experiments. Consequently, relating theoretical predictions to experimental swelling data generally requires an additional conversion step, making the comparison with gravimetric measurements less direct.

Furthermore, many advanced diffusion models have been developed for reactive systems, where solvent transport is coupled with simultaneous chemical reactions or network formation processes [15]. Although these formulations provide a comprehensive description of reactive hydrogels, they are not directly applicable to conventional non-reactive hydrogel swelling, in which water uptake is predominantly governed by diffusion through an already established polymer network [16]. Therefore, there remains a clear scientific gap for an analytical framework that bridges the gap between the rigorous physical grounding of Fick's second law and the practical directness of empirical gravimetric fitting.

To address these limitations and bridge the gap between classical theoretical diffusion models and empirical gravimetric measurements, this study proposes a reformulated diffusion-controlled analytical model for polymeric hydrogel swelling based on one-dimensional Fickian transport. Unlike the classical Crank formulation that predicts normalized water uptake (M_t/M_∞) [17], the proposed model extends the analytical series solution to derive an explicit, closed-form expression for the time-dependent swelling degree, $S(t)$. This reformulation directly links theoretical predictions using only two physically meaningful parameters, namely the effective diffusion coefficient (D) and the equilibrium swelling degree (S_{eq}). Finally, the model is evaluated through numerical simulations and qualitative comparison with swelling trends reported in the literature.

2. Methodology

2.1. Physical Model Assumption

The theoretical model considers the hydrogel as a plane slab with an initial total thickness L, where the lateral dimensions are sufficiently larger than L so that water transport is effectively one-dimensional along

the thickness direction ($0 \leq z \leq L$) [18]. Water diffusion within the polymer network follows Fick's second law with a constant effective diffusion coefficient D, accounting for the free-volume and tortuosity effects of the matrix [9]. The hydrogel surfaces ($z = 0$ and $z = L$) are assumed to be in continuous contact with excess solvent, maintaining a constant equilibrium concentration c_0, while the initial water concentration inside the dry gel is zero. L is taken as the initial, dry-state thickness of the slab and is treated as a fixed effective thickness throughout the diffusion process. The model does not account for the increase in physical thickness that accompanies swelling. No irreversible chemical reactions or degradation processes occur during diffusion, distinguishing the present approach from reactive diffusion models [15]. Furthermore, the polymer network is assumed to swell isotropically, and the macroscopic swelling degree is taken to be directly proportional to the total water uptake per unit dry mass [19]. The proportional relationship between the macroscopic swelling degree and water uptake is generally valid under low to moderate swelling conditions, where the polymer network undergoes approximately isotropic deformation and remains within the linear swelling regime [20]. At high swelling ratios, large deformation and polymer network relaxation may lead to nonlinear swelling behavior [21], limiting the applicability of the linear assumption. The model assumptions are illustrated in Figure 1.

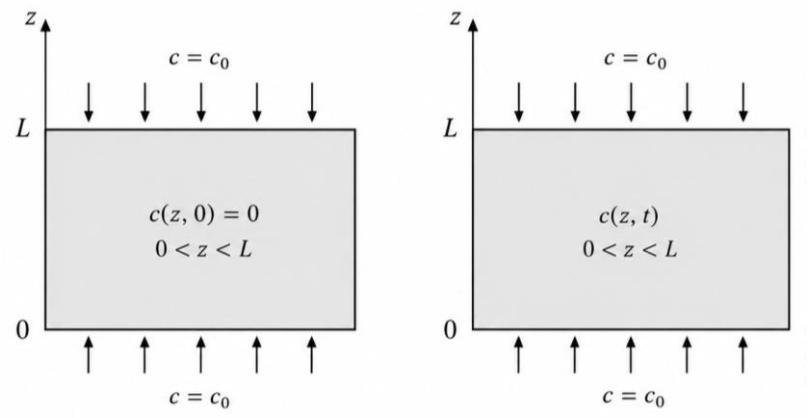

Figure 1. Schematic illustration of the diffusion-controlled swelling model for a hydrogel slab. (a) Initial dry state at $t = 0$, where the water concentration inside the gel is zero, $c(z, 0) = 0$. (b) Hydrated state at $t > 0$, where water diffuses into the hydrogel from both surfaces maintained at the equilibrium concentration c_0. The arrows denote the water solvent, while the rectangle denotes the hydrogel slab.

It should be noted that, although the hydrogel physically swells during hydration, the present model does not explicitly consider the deformation of the gel geometry. Instead, the diffusion problem is solved in a fixed domain of thickness L, and the swelling degree is assumed to be directly proportional to the total water uptake. This fixed-domain approximation follows the classical Crank treatment for diffusion in plane sheets [9].

2.2. Mathematical Model and Analytical Solution

Under the assumptions above, the water concentration *c(z,t)* within the hydrogel satisfies the one-dimensional Fickian diffusion equation:

$$\frac{\partial c(z,t)}{\partial t} = D\frac{\partial^2 c(z,t)}{\partial z^2} \tag{1}$$

where c [kg.m^{-3}] is the local water concentration, t [h] is time, z [m] is the spatial coordinate across the gel thickness, and D [m^2.h^{-1}] is the effective diffusion coefficient.

The associated initial and boundary conditions are:

$$c(z,0) = 0, 0 < z < L \tag{2a}$$
$$c(0,t) = c_0, t > 0 \tag{2b}$$
$$c(L,t) = c_0, t > 0 \tag{2c}$$

where c_0 is the equilibrium water concentration at the gel surface.

To solve Eq. (1) subject to conditions (2a–2c), the solution is decomposed into a steady-state component and a transient component [22]:

$$c(z,t) = c_0 + v(z,t) \tag{3}$$

Substituting Eq. (3) into Eq. (1), the transient component v(z, t) satisfies:

$$\frac{\partial v}{\partial t} = D\frac{\partial^2 v}{\partial z^2} \tag{4}$$

with homogeneous boundary conditions:

$$v(0,t) = 0, \qquad v(L,t) = 0, \qquad v(z,0) = -c_0 \tag{5}$$

Applying separation of variables, we write $v(z,t) = Z(z)\,T(t)$, which yields two ordinary differential equations:

$$\frac{d^2Z}{dz^2} + \lambda^2 Z = 0 \tag{6}$$

$$\frac{dT}{dt} + D\lambda^2 T = 0 \tag{7}$$

The spatial eigenfunctions satisfying the homogeneous boundary conditions in Eq. (6) are:

$$Z_n(z) = \sin\left(\frac{n\pi z}{L}\right), \quad n = 1,2,3, \ldots \tag{8}$$

with corresponding eigenvalues $\lambda_n = \frac{n\pi}{L}$. The time-dependent part is:

$$T_n(t) = B_n e^{-D\lambda_n^2 t} = B_n e^{-\frac{Dn^2\pi^2 t}{L^2}} \tag{9}$$

The general solution for $v(z,t)$ is therefore the Fourier sine series:

$$v(z,t) = \sum_{n=1}^{\infty} B_n \sin\left(\frac{n\pi z}{L}\right) e^{-\frac{Dn^2\pi^2 t}{L^2}} \tag{10}$$

Applying the initial condition $v(z,0) = -c_0$, the Fourier sine coefficients is computed by exploiting orthogonality:

$$B_n = \frac{2}{L}\int_0^L (-c_0)\sin\left(\frac{n\pi z}{L}\right) dz$$

$$B_n = -\frac{2c_0}{n\pi}[1 - (-1)^n]$$

$$B_n = \begin{cases} -\dfrac{4c_0}{(2m-1)\pi}, & n = 2m-1 \\ 0, & n = 2m \end{cases} \tag{11}$$

Retaining only odd-index terms ($n = 2m - 1$, m = 1, 2, 3, …), the full solution for $c(z,t)$ is:

$$c(z,t) = c_0\left[1 - \frac{4}{\pi}\sum_{m=1}^{\infty}\frac{1}{2m-1}\sin\left(\frac{(2m-1)\pi z}{L}\right)e^{-\frac{(2m-1)^2\pi^2 Dt}{L^2}}\right] \tag{12}$$

This result is consistent with the classical solution of the diffusion equation for a plane sheet reported by Crank [9].

2.3. Total Water Uptake dan Swelling Degree

The total mass of water absorbed per unit area of the gel at time *t* is obtained by integrating $c(z,t)$ over the thickness:

$$M_t = \int_0^L c(z,t)\, dz \tag{13}$$

Substituting Eq. (12) into Eq. (13) and integrating term by term:

$$M_t = c_0 L \left[1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{-\frac{(2n+1)^2 \pi^2 Dt}{L^2}} \right] \tag{14}$$

where the index $n = m - 1 \geq 0$ has been used. The equilibrium water uptake ($t \to \infty$) is $M_\infty = c_0 L$, so the normalized fractional uptake is:

$$F(t) = \frac{M_t}{M_\infty} \to F(t) = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{-\frac{(2n+1)^2 \pi^2 Dt}{L^2}} \tag{15}$$

This is the well-known Crank series for diffusion into a plane sheet [9].

The swelling degree *S(t)* [%] is defined experimentally as:

$$S(t) = \frac{W_t - W_d}{W_d} \times 100\% \tag{16}$$

where W_t is the wet mass at time t and W_d is the dry mass of the gel. Since, under the isotropic swelling assumption, the absorbed water mass is proportional to the water concentration integrated over the volume, and the equilibrium value is S_{eq}, and is obtained the central model equation:

$$S(t) = S_{eq} F(t)$$

$$S(t) = S_{eq} \left[1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{-\frac{(2n+1)^2 \pi^2 Dt}{L^2}} \right] \tag{17}$$

Equation (17) constitutes the diffusion-controlled swelling model. It expresses *S(t)* entirely in terms of two physically interpretable parameters: (i) S_{eq}, the equilibrium swelling degree determined by polymer–solvent thermodynamics and cross-link density, and (ii) D/L^2, a diffusional rate parameter and Dt/L^2, a dimensionless diffusivity that controls the timescale of approach to equilibrium.

2.4. Short-Time dan Long-Time Apporximation

For short times $\left(\frac{Dt}{L^2} \ll 0.1\right)$, the Fourier series converges slowly and it is more convenient to use the short-time approximation derived from a semi-infinite medium assumption [9].

$$S(t) \approx S_{eq} \times \frac{4}{L} \sqrt{\frac{Dt}{\pi}} \tag{18}$$

Equation (18) predicts that the initial swelling rate is proportional to $t^{1/2}$, the hallmark of Fickian (Case I) diffusion. This linear relationship between *S* and $t^{1/2}$ is widely used experimentally to extract *D* from early-time swelling data [23].

For long times $\left(\frac{Dt}{L^2} \gg 0.1\right)$, the series in Eq. (17) is dominated by the first term ($n = 0$), giving:

$$S(t) \approx S_{eq} \left[1 - \frac{8}{\pi^2} e^{-\frac{\pi^2 Dt}{L^2}} \right] \tag{19}$$

From Eq. (19), a semi-logarithmic plot of $\left(1 - \frac{S(t)}{S_{eq}}\right)$ versus t should be linear at long times, with a slope of $-\frac{\pi^2 D}{L^2}$ from which *D* can be independently estimated.

2.5. Numerical Evaluation

Equation (17) is evaluated numerically using the Python programming language with the NumPy library. The infinite series is truncated at N = 50 terms, which is sufficient for convergence to better than 10^{-6} relative error over the range of Dt/L^2 explored in this study; at very short times ($Dt/L^2 \ll 0.01$) the series converges slowly, which is why the short-time approximation of Eq. (18) is used instead in that regime, consistent with standard practice for this class of series. The independent variable is time $t \in [0, 50]$ hours, and two sets of parametric studies are conducted: (a) varying D/L^2 ² over the range 0.05–1.50 h^{-1} with fixed S_{eq} = 200%, and (b) varying S_{eq} over the range 80–330% with fixed $D/L^2 = 0.30$ h^{-1}. Additionally, the normalized water uptake $F(t)$ and the characteristic time to reach 90% of equilibrium swelling (t_{90}) are computed as a function of D/L^2 over the range 0.01–5 h^{-1}. All comparisons with literature swelling data are qualitative, trend-level comparisons rather than direct least-squares fits, since the literature sources used report equilibrium swelling ratios and qualitative kinetic trends rather than complete digitized $S(t)$ datasets suitable for fitting.

3. Results and Discussion

3.1. The Diffusion-Controlled Swelling Model

The core result of this study is Eq. (17), which provides an explicit analytical expression for the time-dependent swelling degree $S(t)$ of a planar hydrogel slab undergoing Fickian water diffusion. The derivation follows the classical approach of Crank [9], for solving the diffusion equation in a finite plane sheet, adapted to the context of hydrogel swelling by expressing the total water uptake in terms of the experimentally accessible swelling degree metric.

The physical interpretation of the two model parameters is straightforward. The equilibrium swelling degree S_{eq} represents the maximum water absorption capacity of the gel at thermodynamic equilibrium, where the osmotic driving force for water uptake is exactly balanced by the elastic restoring force of the cross-linked network. According to the Flory–Rehner theory [24], S_{eq} depends inversely on the cross-link density ν_e and on the Flory–Huggins parameter χ. Gels with low cross-link density (fewer chemical or physical junction points per unit volume) exhibit high S_{eq}.

The diffusion coefficient D characterizes the rate of water transport through the polymer matrix. It is influenced by the free-volume available for water mobility, the polymer–water friction coefficient, and the degree of swelling itself. In a constant-D (Fickian) model, D is treated as an average value over the entire swelling process. The parameter D/L^2 (units: h^{-1}) is the natural timescale parameter; larger D/L^2 implies faster equilibration.

The present model differs fundamentally from the reactive diffusion framework applied to edible electronic materials [15], in which water diffusion is coupled to an irreversible first-order interfacial reaction (characterized by a rate constant k). In that context, the governing PDE takes the form:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2} - kc \tag{20}$$

The reaction sink term $-kc$ in Eq. (20) leads to exponentially decaying concentration profiles and a monotonically decreasing material thickness over time. In contrast, for hydrogel swelling there is no consumption of water by chemical reaction; water merely redistributes from the bulk solution into the polymer network. The relevant PDE is therefore the pure diffusion equation (1), without a reaction term, and the long-time behavior approaches a finite equilibrium rather than complete dissolution.

3.2. Effect of Difussion Coefficient on Swelling Kinetics

Figure 2(a) shows the predicted swelling degree $S(t)$ as a function of time for six values of the D/L^2, ranging from 0.05 to 1.50 h^{-1}, with S_{eq} fixed at 200%. All curves exhibit the characteristic sigmoidal shape observed experimentally [7], [25], [26]: an initial rapid increase at short times, a gradual transition, and an asymptotic approach to S_{eq}.

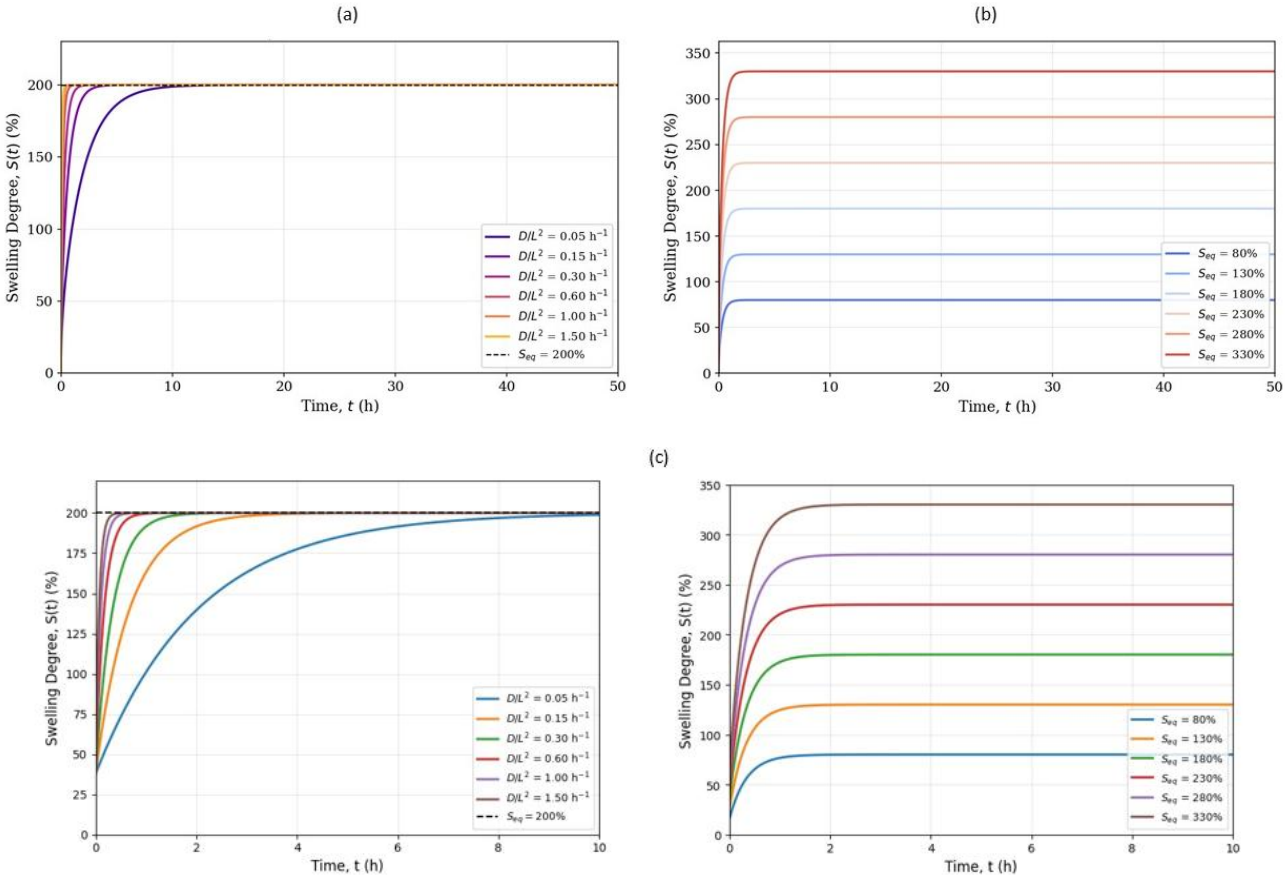

Figure 2. Predicted swelling degree *S(t)* from the diffusion-controlled model (Eq. 17): (a) effect of diffusion coefficient D/L^2 for fixed S_{eq} = 200%; (b) effect of equilibrium swelling degree S_{eq} for fixed D/L^2 = 0.30 h^{-1}; (c) Enlarged view of the predicted swelling degree curves during the first 10 h of swelling.

As D/L^2 increases from 0.05 to 1.50 h^{-1}, the time required to reach equilibrium decreases substantially. For D/L^2 = 0.05 h^{-1}, based on Eq. (17) and plotting graph, the gel requires approximately 5.65 hours to reach 95% of S_{eq}, whereas for D/L^2 = 1.50 h^{-1}, the same level is attained within approximately 0.19 hours. This strong dependence on diffusivity is consistent with the theoretical model. In the early stage of swelling, Eq. (18) predicts that the swelling rate scales with $\sqrt{D}$, leading to a more rapid initial uptake for hydrogels with larger D/L^2 . Importantly, variations in D affect only the kinetics (rate of water uptake) and not the thermodynamic endpoint S_{eq}, which remains constant at 200% across all curves in Figure 2(a).

This behavior is in agreement with experimental observations for cellulose nanocrystal (CNC)-based polyacrylamide hydrogels of varying concentration of CNC. The inverse relationship between crosslinking density and swelling degree arises from the reduction in network mesh size and porosity, which restrict water diffusion and polymer chain mobility. An increase in crosslinking enhances the elastic constraint of the hydrogel network, thereby limiting its equilibrium expansion and resulting in a lower swelling degree [11].

3.3. Effect of Equilibrium Swelling Degree

Figure 2(b) presents the effect of S_{eq} on the swelling curves for a fixed D/L^2 = 0.30 h^{-1}. As S_{eq} increases from 80% to 330%, the equilibrium plateau shifts proportionally, while the shape of the normalized swelling curve $F(t) = \frac{S(t)}{S_{eq}}$ remains identical for all cases, a direct consequence of the linear scaling in Eq. (17). This linearity implies that the model predicts a universal normalized kinetic curve $F(t)$ that depends only on D/L^2, regardless of the specific gel composition, provided Fickian diffusion holds.

The proportionality between the absolute swelling rate (dS/dt) and S_{eq} follows directly from differentiating Eq. (17):

$$\frac{dS}{dt} = S_{eq}\left(\frac{8D}{L^2}\right)\sum_{n=0}^{\infty} exp\left(-\frac{(2n+1)^2\pi^2 Dt}{L^2}\right) \quad (21)$$

At $t = 0^+$ (represents the moment immediately after the swelling process starts), the series in Eq. (21) diverges (consistent with the square-root singularity in Eq. 18), indicating an instantaneous very high initial uptake rate at the surface. In practice, this singularity is regularized by the finite sample preparation time and any surface film resistance, but for most experimental systems the early-time behavior does closely follow the $t^{1/2}$ scaling [11].

3.4. Normalized Water Uptake and Swelling Timescale

Figure 3(a) shows the normalized water uptake $F(t) = \frac{M_t}{M_\infty} = \frac{S(t)}{S_{eq}}$ as a function of time for five values of D/L^2. The universal character of $F(t)$ is evident: regardless of S_{eq}, all hydrogels with the same D/L^2 follow identical normalized kinetics. The curves are bounded between 0 and 1, with the rate of approach to unity increasing monotonically with D/L^2.

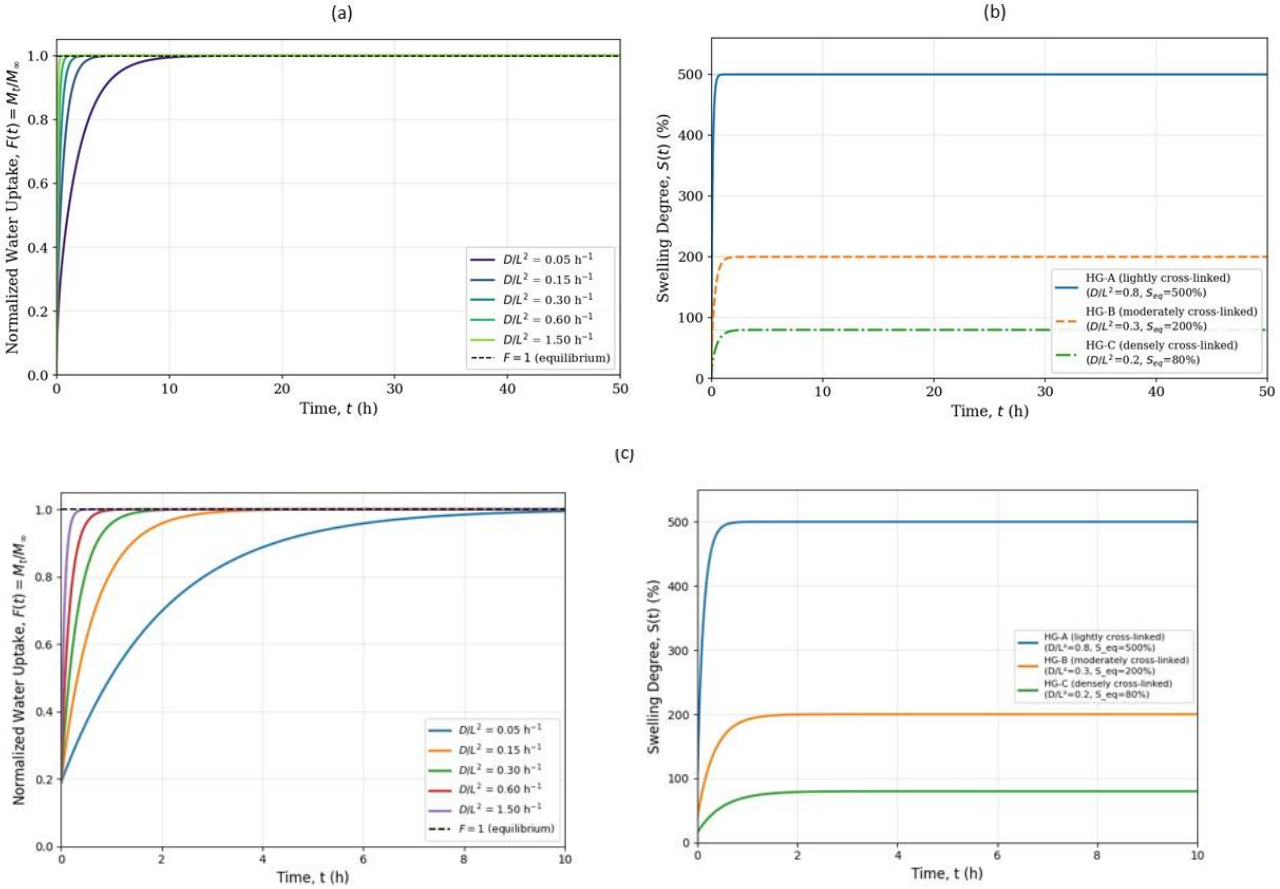

Figure 3. (a) Normalized water uptake $F(t) = M_t/M_\infty$ vs. time for different values of D/L^2. (b) Predicted swelling degree $S(t)$ for three illustrative hydrogel categories with different cross-link densities. (c) Enlarged view of the first 10 h of normalized water uptake and predicted swelling degree.

Figure 3(b) illustrates model predictions for three illustrative hydrogel categories: a lightly cross-linked network (HG-A, D/L^2 = 0.80 h^{-1}, S_{eq} = 500%), a moderately cross-linked network (HG-B, D/L^2 = 0.30 h^{-1}, S_{eq} = 200%), and a densely cross-linked network (HG-C, D/L^2 = 0.20 h^{-1}, S_{eq} = 80%). %). These three parameter sets are chosen only to illustrate the qualitative trend that lower cross-link density is generally associated with higher D/L^2 and higher S_{eq} and are not fitted to a specific experimental dataset. D and S_{eq} are treated as independent parameters here for illustration only. In real hydrogels, changes in composition or cross-link density typically affect both parameters simultaneously, so the HG-A, HG-B, and HG-C curves are represented as illustrative cases. The model prediction is qualitatively consistent with the experimental trend that increasing the CNC content from 0 to 3 wt.% decreases the swelling ratio from 11.69 g g^{-1} (PAm) to 10.87 g g^{-1} (PAC1) and 10.33 g g^{-1} (PAC2). The incorporation of CNC promotes additional physical crosslinking through intermolecular hydrogen bonding, leading to a more compact polymer network with smaller mesh sizes and reduced porosity [11].

3.5. Characteristic Swelling Timescale

Figure 4 shows the time required to reach 90% of the equilibrium swelling degree (t_{90}) as a function of D/L^2 on a semi-logarithmic scale. The relationship is hyperbolic: t_{90} decreases steeply for small D/L^2 and approaches zero asymptotically for large D/L^2. This reflects the fundamental scaling $t_{90} \propto L^2/D$, which shows that the characteristic diffusion time scales with the square of the sample thickness and inversely with the diffusion coefficient [9].

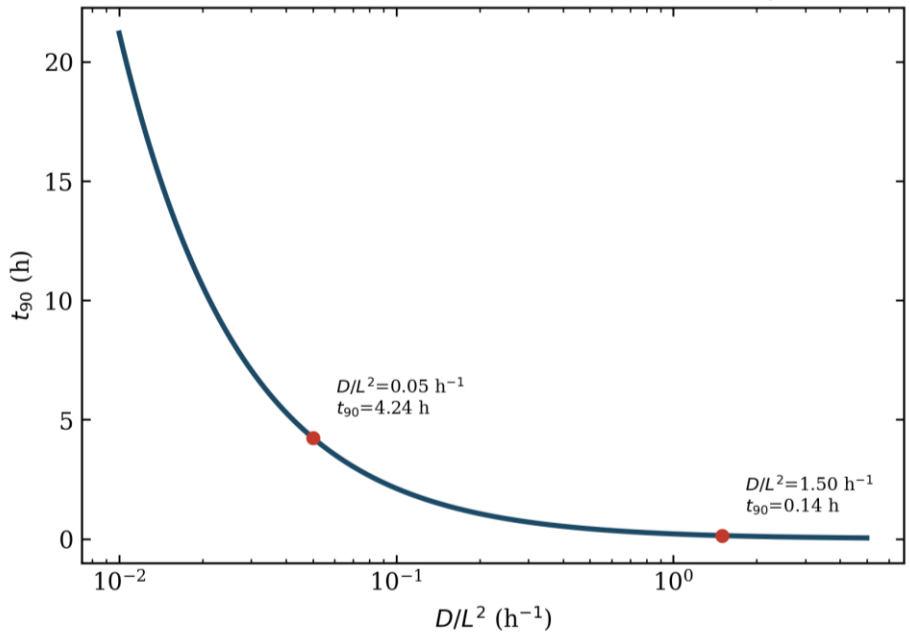

Figure 4. Characteristic time t_{90} (time to reach 90% of equilibrium swelling) as a function of Diffusional rate parameter D/L^2.

From a practical standpoint, Figure 4 can be used as a design chart: given a target swelling timescale t_{90} and a gel thickness L, the required diffusion coefficient D can be directly read off. Conversely, for a known D (e.g., estimated from molecular dynamics simulations or pulsed-field-gradient NMR measurements), the optimal gel thickness for a desired response time can be determined. This has direct implications for the design of controlled-release drug carriers, where the time window for drug liberation is tied to the swelling rate, and for responsive actuators, where rapid swelling is required for actuation speed [27], [28].

3.6. Comparison with Experimental Data and Model Limitations

The diffusion-controlled model (Eq. 17) reproduces the qualitative features of hydrogel swelling observed in the literature, in particular the characteristic rapid initial uptake followed by a plateau approach to equilibrium. Several groups have reported swelling kinetics that conform to the Fickian solution: Tippabattini et al. for conducting Polyacrylamide–Cellulose Nanocrystal hydrogels for smart materials in the field of controlled drug delivery applications [11], Hanife et al. for chitosan hydrogel [29]. In all these cases, the swelling curves exhibit the characteristic rapid initial uptake followed by a plateau, consistent with Figure 1 and Figure 2 of the present study.

Quantitatively, the model requires knowledge of two parameters (D and S_{eq}) which can be determined by fitting to experimental $S(t)$ data. S_{eq} is directly measured from the long-time plateau, and D is extracted from either the short-time linear region in a S vs. $t^{1/2}$ plot (Eq. 18) or from the long-time exponential decay slope in a $\ln\left(1 - \frac{S}{S_{eq}}\right)$ vs. t plot (Eq. 19). Typical values of D for synthetic hydrogels range from 10^{-13} to 10^{-11} m^2 s^{-1} [17], [30], corresponding to $D/L^2 \approx 0.1$–2.0 h^{-1} for millimeter-scale gel slabs, consistent with the parameter ranges explored in this study.

The model does have important limitations. First, the assumption of constant D is violated in systems exhibiting anomalous (non-Fickian) diffusion, which is common in glassy polymers and gels with concentration-dependent mobility. In such cases, the swelling exponent n in the Korsmeyer–Peppas power law $S \propto t^n$ deviates from 0.5 (Fickian) toward 1.0 (Case II or relaxation-controlled) or intermediate values [31]–

[33]. Second, the plane-sheet geometry may not be appropriate for spherical or cylindrical hydrogel beads, which would require the corresponding spherical or cylindrical Crank solutions [9]. Third, the model does not account for the coupling between swelling-induced mechanical stress and diffusion transport (poroelastic coupling), which can slow diffusion in highly swollen gels [34]. Finally, temperature effects on both D and S_{eq} are not explicitly included, though they could be incorporated through Arrhenius-type dependences [35]. Lastly, because the comparisons in this study are limited to qualitative trends rather than direct fits to digitized experimental *S(t)* data, the present results should be regarded as a demonstration of the model's plausibility rather than a quantitativevalidation; a dedicated fitting study against controlled experimental datasets is left for future work.

Although the model has several limitations, Eq. (17) provides a physically based a physically based analytical approach that is qualitatively consistent with reported hydrogel swelling behavior. It serves as an intermediate framework between empirical models and fully coupled poroelastic formulations, combining mathematical simplicity with a physically interpretable parameterization.

4. Conclusions and Recommendations

This study developed a diffusion-controlled analytical model for hydrogel swelling based on one-dimensional Fickian diffusion in a planar geometry. The model yields a closed-form expression for the swelling degree, $S(t)$, in terms of the equilibrium swelling degree (S_{eq}) and the effective diffusion coefficient (D). Unlike the conventional Crank formulation, which primarily describes normalized or relative water uptake kinetics, the proposed formulation expresses the diffusion process directly in terms of the swelling degree, *S(t)*, thereby establishing a direct analytical link between diffusion kinetics and gravimetric swelling measurements. The formulation retains the characteristic Fickian relationship at short times, while the results show that increasing D/L^2 accelerates the approach to equilibrium, whereas S_{eq} determines the equilibrium swelling capacity. These predicted trends are qualitatively consistent with swelling behaviors reported for hydrogel systems in the literature. The proposed model is applicable to diffusion-controlled swelling under the assumptions of one-dimensional transport in a planar hydrogel with constant effective diffusivity. Within this scope, the model may offer a simple starting point for interpreting hydrogel swelling kinetics. Future work may extend the model to account for non-Fickian transport, concentration-dependent diffusivity, complex geometries, and poroelastic coupling between solvent transport and polymer network deformation and quantitative validation against fitted experimental data.

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