

Modelling and Simulation of Hydro-gel Growth Mechanism by Analysis of Experimental Data

Priyadarshi Majumdar^{a, b*}

^a Jyotinagar Bidyasree Niketan H.S. School, 41 Jyotinagar, Kolkata 700108, India

^b GET IIT-JEE, BE 89, SEC: I, Salt Lake City, Kolkata 700064, India

Abstract We have experimentally studied the growth process of a water-absorbing polymer commonly known as hydro-gel. We took a number of spherical beads, immersed them in pure water, measured their diameters at regular intervals of time and plotted graphs showing the change in volume with the time of immersion, to analyze their swelling properties. We have formulated a dynamical model on the basis of curve-fitting to our experimental data. Our mathematical modelling is devoted solely towards the explanation of the swelling of spherical hydro-gels and we have interpreted our observations on these basis. And finally evaluating the constants of the process, we have shown that the results obtained from our modelling and numerical simulation exactly match the experimental data. The justification of this new approach lies in its successful application for the complete explanation of our observations through numerical and analytical ways.

Keywords: Hydro-gel; Experimental growth study; Mathematical modelling; Numerical analysis.

INTRODUCTION

The hydro-gel or water-gel polymers are basically poly-acryl amide (PAA) ($(-\text{CH}_2\text{CHCONH}_2)_n$), an odorless water-absorbing super-absorbent polymer capable of growing at a fast rate to a huge size when immersed into water. PAA's may crystallize but normally this type of commercial beads are either amorphous or polycrystalline. In fact, they may absorb water upto a maximum of 150–300 times their weight. Because of their incredible thirst, they are even used to reduce the amount of water needed for water crops and also as a source of water in gardens during drought. These polymer gels are non-toxic moisture retaining soil additives (also they are neutral in pH). Under dry conditions these synthetic polymer gels form tiny beads. Polymer gels absorb liquid fertilizer just as they do water hence serving as food storage reservoirs in the soil. As the polymer gels expand and contract responding to water availability, they aerate the soil. They may be of several colors. This polymer chain contains a large number of charges which attract the H_2O molecules in ionized forms. When immersed in water, the volume of each bead is found to increase for a certain period of time (depending upon the number of absorbing units) and then it asymptotically saturates towards a maximum value. As these solid hard beads absorb water they become soft, gel-like. The rate of increase in volume is quite large initially; it gradually slows down and finally decreases to zero. The absorption of water in hydro-gels are caused due to their cross-linked polymer network structure^[1] having the ability to store water in the inter-polymer chain pores. The existing explanatory works^[2] on hydro-gel uses this principle of cross-linking. In a numerical study of the diffusion process^[3] the mass-diffusion and the swelling capacity were found to decrease with increasing nominal cross-linking ratio. Some studies^[1, 4] deal with the Fick's equation, analyzing the diffusion of solutes through

* Corresponding author: P. Majumdar, E-mail: majumdar_priyadarshi@yahoo.com

Received May 28, 2013; Revised July 5, 2013; Accepted July 8, 2013

doi: 10.1007/s10118-014-1405-1

polymer matrices and are used to model such systems. The diffusion coefficients (dc) of solutes through a diffusible polymer matrix are experimentally determined^[5] in double cell diffusion apparatus. The same work^[5] also shows that the dc has linear relation with time where the structure, pore size and polymer composition of gel are taken into account. The swelling by Fickian and non-Fickian mechanism in diffusion characteristics has also been studied in some other relevant works^[2, 6, 7]. In particular, some studies^[8, 9] use numerical computation to determine the diffusion coefficients of these hydro-gels for the Fickian mechanism.

Most of the studies on hydro-gels were mainly experimental. The isotherms were plotted and analyzed thereby^[5, 6]. On the other hand in our present framework we have performed a simple in-house experiment with the hydro-gel beads. Our main purpose in this work is to explain the corresponding experimental plots on the basis of analytical modelling and numerical analysis of our collected data. We have shown that our theoretical curves almost fit the experimental plots. Also we predicted some empirical relations and dynamical equations of the water absorption process. Finally our curves are compared with some other experimental results and the correspondence between them may be noted.

Moon *et al.*^[10] studied the preparation and properties of biodegradable hydro-gels and the swelling and de-swelling behaviors under different conditions (cross-linking density of the reagent, pH of the water solution *etc.*). In particular they^[10] examined the variation of swelling ratio $q(t)$ (the ratio of the weight of the water content in the swollen hydro-gel to the weight of dry hydro-gel (W_0) at any instant t during the process of swelling) with temperature and time.

$$q(t) = \frac{W_t - W_0}{W_0} \quad (1)$$

where W_t is the weight of the swelling hydrogel at time t .

The nature of variation obtained is almost similar to that of ours. In a similar work (preparation and swelling) Min *et al.*^[11] have also worked with the biodegradable hydro-gels and plotted similar kind of graphs. Kunioka^[12] studied the biodegradable hydro-gels from their preparation point of view and also the degree of swelling with variation of pH and time. Alaei *et al.*^[13] discussed the application of hydro-gels as humidity absorbents for drying of natural gas and oil products like gasoline and kerosene. Peng *et al.*^[14] studied the swelling properties of hydro-gel-elastomer composite biomaterials from the preparation, mechanical properties and swelling stability. Karadag *et al.*^[15] examined the swelling property of gamma-radiation cross-linked poly hydro-gels and they have shown that the weight swelling ratio actually obeys the relation

$$t / q(t) = A + B t \quad (2)$$

under equilibrium $q = 0$ at $t = 0$. The variable $q + 1 = W_t/W_0$ thus denotes the ratio of weights of the swollen hydro-gel to the dry hydro-gel at temperature t . This equation tells us that at $t \rightarrow \infty$ we have $q \rightarrow (1/B)$ (maximum swelling ratio) and as $t \rightarrow 0$, $dq/dt = 1/A$ (initial rate of variation of swelling ratio). Also we may define the swelling power

$$P_{\text{swelling}} = \frac{W_t}{W_0} = q + 1 = Kt^s \quad (3)$$

K and s are the swelling constant and swelling (diffusional) exponent respectively. The latter one is an indicative of the transport mechanism. The validity of Eq. (3) will be up to the instant of 60% swelling for any bead^[15]. Fickian diffusion and Case II transport are defined for $s = 0.5$ and $s = 1$ respectively^[15], whereas anomalous transport behavior (non-Fickian diffusion) is of intermediate character between Fickian and Case II and will be valid for $0.5 < s < 1$ ^[15].

In comparison with the traditional diffusion and swelling studies including both Fickian type^[1, 4] as well as on lattice model due to Smolochovski^[16] and Langevin^[17] what we have done new in our present work, is the generation of a mathematical lattice model (with a set of normalized data) which is sound in physical arguments

and also fits our experimental data regarding the growth (swelling) process of hydro-gel beads not as complex as those mentioned^[16, 17]. As a summary, our study is not merely an arbitrary curve fitting to a set of primary data but something more than that. The mathematics we have derived here may be taken as the governing equations regarding the swelling process of hydro-gel.

The existing literatures on the swelling properties of hydro-gels or water-gels deal with different experimental studies involving diffusion of liquid into solid objects, the parameters involved therein and the different graphical plots regarding those data. We have already mentioned this fact earlier. In our present approach we have adopted experimental and theoretical techniques equipped with strong physical basis and efficient numerical computation, eliminating any need of using the standard mass diffusion technique involving Fickian or any other mechanism. In particular we consider the porous hydro-gel as a 3d lattice structure, the lattice elements being the sites capable of absorbing exactly one hydro-gel bead. From our present model we have established Eq. (2) and Eq. (3) with the evaluation of the corresponding parameters.

Experimental Setup with Material and Method

We made here an experimental study of the growth process of water-absorbing polymers. In particular we took a number of tiny spherical beads and measured their initial mean diameters (d) (corresponding initial volume of the bead is v). We then immersed the beads into purified water and measured their mean diameters again up to the highest attainable diameter (D) within our experimental time (T_{exp}). Quite understandably T_{exp} may never be as large as possible. We measured mean diameters because the beads may not be exactly spherical in shape during their growth process. The time intervals were each of thirty minutes. The measurement process was performed under identical conditions, taking them out from water quickly and again throwing them into the water (the temperature during the entire experiment was tried to be kept constant by performing it under identical conditions all throughout). For the purpose of diameter measurement we used a slide-caliper having vernier constant 0.01 cm. The time interval between two successive measurements was chosen in such a way that the time required for a single measurement should become negligible in compare to it. It certainly minimized the discreteness in the growth process. In fact we took five sets of transparent beads each set had a particular initial diameter unique to it and ranging from 1 mm to 4 mm (having the same chemical compositions and properties). In addition to the diameter or volume measurement we have also measured the initial mass (m) (in dry condition) and the almost maximum (M'_{max}) swollen mass of the beads using a simple balance. To minimize the error in the mass measurement process we again took a large number of identical beads and measured their total mass. Same procedure has been adopted in the diameter measurement process such that when mass and diameter data sets were normalized (the total mass was scaled down with the number of beads and the time-diameter data for the large sample was normalized for statistical errors) they gave us the data corresponding to a single bead. The process of diameter measurement at regular intervals during swelling of each bead was continued up to the point where beads almost reached their respective maximum volumes (V'_{max}). We ensured this pre-maximization by measuring the diameters of the beads for a few more time intervals (again of 30 min.) and observing that there was only a negligible growth. Hence, for all practical purposes, we may assume that the highest measured volume or mass within our experimental time (T_{exp}) was equal to those values corresponding to the time instant T_{exp} . On the contrary for a direct measurement of water absorbed by each bead we used a volumetric cylinder as the water container. The large sample size of identical beads again served (using normalization technique) to minimize the error in the computation of the decrease in volume of the water content of the cylinder from its calibrations. Because when the beads were taken out from the cylinder every time a thin layer of water was attached to their surfaces.

Finally we plot a graph (Fig. 1) between the volume (V) of the beads in mL and the corresponding time of immersion inside water (t) in hour (the discrete data plots are corresponding to the time instants of diameter-measurement), the immersion-time for the beads are 2 h to 8 h depending upon the initial size of the beads. The experimental mean data (normalized) regarding the diameters of five different transparent beads (varying in diameters) have been presented in Table 1 below. And the data corresponding to the last row of each column will

give us the initial (v) as well as the final experimental volumes ($V'_{\max}$) of the beads and the experimental maximum times (T_{exp}) of their immersion.

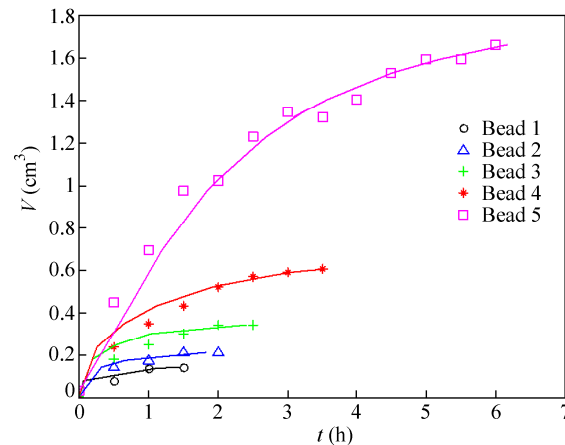


Fig. 1 Experimental mean data plot (normalized) during the water absorption for five different transparent beads. Beads are of variable initial size. The solid lines along those plots are showing the possible fits to those graphs generated from our modelling and numerical analysis (to be discussed later on).

Table 1. Diameter of hydro-gel versus time

Time (min)	Bead 1 (cm)	Bead 2 (cm)	Bead 3 (cm)	Bead 4 (cm)	Bead 5 (cm)
0	0.17	0.20	0.23	0.29	0.40
30	0.53	0.60	0.65	0.74	0.95
60	0.62	0.69	0.75	0.82	1.10
90	0.64	0.74	0.83	0.94	1.23
120		0.75	0.85	1.00	1.25
150			0.86	1.02	1.33
180				1.03	1.36
210				1.04	1.37
240					1.39
270					1.43
300					1.45
330					1.45
360					1.47

In Fig. 2(a) we have plotted t/q against t , Fig. 2(b) shows the variation of $\ln(q + 1)$ against $\ln(t)$. The fact that both these plots have linear nature may be explained using Eqs. (2) and (3) (with q defined by Eq. (1)). The experimental plots in both Fig. 1 and Fig. 2 are shown by data points only and not by the continuous lines; they are the fits to those data which we mentioned already. We then sought to explain those plots using some mathematical modelling formulation following the dynamics of the process and thereafter fit curves to the experimental data of Fig. 1. The method of determination of q will be described later on.

The measured parameters in our experiments are the variable diameters of the beads and the time of swelling, the corresponding instruments are a simple vernier calipers and a simple watch (our time intervals are of the order of half an hour or so, hence we did not use a stop watch) respectively. The possible absolute error in the diameter measurement process was of the order of the vernier constant of the instrument (0.01 cm.). The absolute error in the time measurement process may be less than one min.

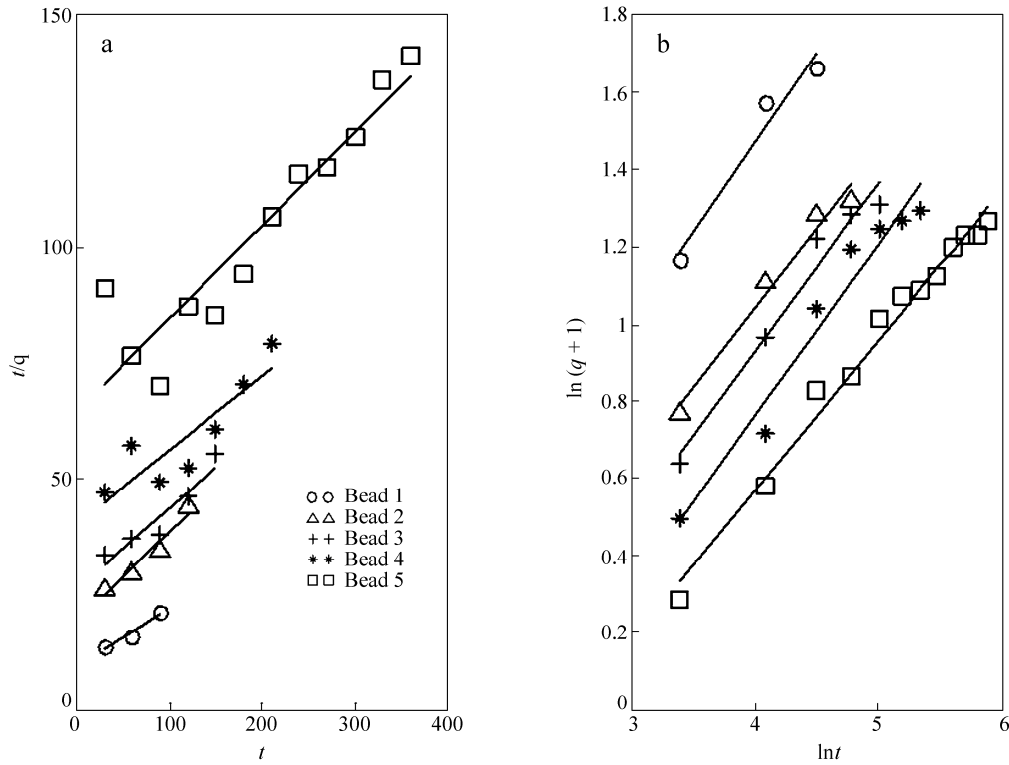


Fig. 2 Experimental data plot of weight-swelling ratio versus time for five different beads: (a) ratio of time (t) in h and weight-swelling ratio (q) against t in h, (b) $\ln(q+1)$ plotted against $\ln(t)$ in h. The solid lines about those plots are showing the possible fits to those graphs generated from our analysis.

Proposed Theoretical Model with Experimental Findings

The growth process of hydro-gels, is a swelling process, where polymer chains on the surface of hydro-gel beads will swell first, and then those polymer chains inside the ball follow. Once the polymer chains on the surface fully swell, they will not be active anymore in absorbing water. But this doesn't mean that the whole swelling process is finished, the polymers inside the ball might still absorb water. But when the polymer chains on the outer surface of hydro-gel ball swell completely, they will not absorb water anymore. The absorption layer now should move inside the bead.

Let v be the volume of a single solid spherical bead under dry condition (before immersing it into water) while N being the total number of sites in the bead, capable of absorbing water molecules. At any point of time t , $n(t)$ indicates the number of water molecules attached to the bead. Thus $N_c(t) = N - n(t)$ is the total number of available absorbing centers at time t or the number of water molecules those can still be absorbed, since according to our assumption one absorbing center may absorb a maximum of single water molecule; as there may be absorbing centers which are not absorbing water molecules at all. We define w as the average increase in volume due to the absorption of a single water molecule. Therefore, the volume (V) of the bead at time instant t is

$$V(t) = v + n(t)w \quad (4)$$

Maximizing both sides we obtain (here unlike the experimental maximum volume $V'_{\max}$, we have the true maximum volume $V_{\max}$)

$$V_{\max} = v + Nw \quad (5)$$

Due to its spherical shape, the surface area (A) may be expressed as

$$A(t) = C_1(v + n(t)w)^{\frac{2}{3}} = C_1V(t)^{\frac{2}{3}} \quad [C_1 = (36\pi)^{\frac{1}{3}}] \quad (6)$$

The diffusion of water into the PAA may only occur through its surface and that also depends upon the number of vacant sites inside the bead. Hydro-gel beads absorb water through their entire surface in contact with water because of the homogeneity of the beads and the liquid. But in the absence of any absorbing centre inside the beads even if in contact with water it will certainly not swell. Keeping in mind these facts we predict that the rate of absorption (dn/dt) depends upon (expectedly) the surface area (A) and the number N_c at t , consequently one may write

$$\frac{dn(t)}{dt} = C_2 A^a N_c^b \quad (7)$$

a and b are two arbitrary scaling exponents controlling the degree of dependence of dn/dt on the quantities A and N_c , also they should be the constants of the process and must not depend upon the size and color of the bead. C_2 is a positive constant because it indicates a growth process. Using Eq. (6) in Eq. (7)

$$\frac{dn}{dt} = C_3(v + nw)^{\frac{2a}{3}} (N - n)^b \quad [C_3 = C_2 C_1^a = C_2 (36\pi)^{\frac{a}{3}}] \quad (8)$$

We may expect that the positive constant C_3 (or C_2) is associated with the chemical properties of the bead (due to its process-independent nature), consequently must remain same for PAA beads of same color and of different size but may vary for different colored beads. The rate of absorption of water molecules must also depend upon two other factors, namely the temperature and pH of the solution. The pH of the water solution may remain constant but its temperature may certainly fluctuate within a short range for the prolonged nature of the experiment and we were not using any constant temperature bath either. It will affect the numerical value of C_3 also. As a result we may not finally obtain C_3 as a property of the material of the beads alone; rather it may also contain an arbitrary fluctuating part related to the possible temperature variation. The fluctuating part must be a dimensionless number since the dimensions of the temperature as well as pH factor-dependent part are balanced on both sides of Eq. (8).

Equation (8) is a differential equation which has to be solved to gather information regarding the variation of n with time t under the boundary condition that at $t = 0$, $n = 0$. Also it is clear that at $n = N$, $dn/dt = 0$. Again using Eqs. (4), (8) may be recast in the form

$$\frac{dV}{dt} = C_3 w V^{\frac{2a}{3}} \left(N - \frac{V - v}{w} \right)^b = C_3 w^{1-b} V^{\frac{2a}{3}} (V_{\max} - V)^b \quad (9)$$

Similar to Eqs. (8), (9) also has to be solved under the boundary condition that at $t = 0$, $V = v$. Again at $V = V_{\max}$, $dV/dt = 0$. Solution to Eq. (9) will give us a complete picture regarding the variation in volume of the hydro-gel with time. In general for any a and b one may solve Eq. (9) to estimate C_3

$$T_{\text{theo}} (V_{\max})^{\frac{2a}{3} + b - 1} C_3 = w^{b-1} \beta \left(1 - \frac{2a}{3}, 1 - b \right) \quad (10)$$

using the definition of the β -function^[21] and with the assumption $v \leq V_{\max}$. Equation (10) is obtained by integrating Eq. (9), taking the time variation from 0 to T_{theo} and volume variation from v to $V_{\max}$. Here T_{theo} denotes the theoretical time needed for the maximization of bead-volume.

In order to estimate C_3 from Eq. (10) or to solve Eqs. (8) and (9) numerically, we should have an order of estimation of the constants w , N , v , a , b and T_{theo} from our experimental observations.

In most of the dynamical growth mechanisms *e.g.* the natural growth processes in the biological world, like those of mass or limb of any organism with time^[18, 19, 20], the nature of growth becomes asymptotic to the final value at the later stages of the growth. Analogically the analytical value of T_{theo} is clearly infinity. But according

to our discussion, the constant C_3 must be process independent. It should be a property of the hydro-gel bead, hence should have some finite value. This may only be achieved if the β -function mentioned in Eq. (10) also tends to infinity. Consequently we may either have $a = 3/2$ or $b = 1$ (using the property of β -function^[21]).

While performing a simple in-house experiment with hydro-gels we observe that the maximizations of volumes take place within a finite span of time because we may never differentiate between the situations of whether the volume has reached $V_{\max}$ or 95% (or so) of $V_{\max}$ even using a well precision instrument. But that will make a big difference in the end. Reaching from 95% to 100% of final volume may take an incredible amount of time (which is infinity in reality). So we introduce a new variable T_{exp} (already introduced in the introduction section), which is the measured (experimental) length of the time interval, at the end of which a particular bead has attained the volume $fV_{\max}$, where f is a fraction whose value is nearly 1. In real processes it may so happen (as mentioned) that $T_{\text{theo}} \geq T_{\text{exp}}$. Also the ratio $v/V_{\max}$ may not always be too small. So the experimental estimate of C_3 (again integrating Eq. (8)) may be

$$C_3 = \frac{w^{b-1}}{T_{\text{exp}} (V_{\max})^{\frac{2a}{3}+b-1}} \left[\sum_{p=0}^{\infty} \prod_{i=0}^{p-1} (b+i) \frac{\left(f^{p+1-\frac{2a}{3}} - \left(\frac{v}{V_{\max}} \right)^{p+1-\frac{2a}{3}} \right)}{\left(p+1-\frac{2a}{3} \right) p!} \right] \quad (11)$$

in which, unlike in Eq. (10), the time variation is now from 0 to T_{exp} . And the variation in volume is from v to $fV_{\max}$. Equation (11) suggests that we must not choose $a = 3/2$ as it will make the $p = 0$ -term to be blown up. Hence we choose $b = 1$ (following the conclusion made from Eq. (10)). That the value of b must remain constant may also be predicted in the following manner. We notice that b is the exponent to $(N - n)$ and the latter is dimensionless, hence apparently we have not much restrictions while choosing b (Only restriction is that b must be positive, since negative b implies that as the vacant space inside the bead decreases the rate of intake of water molecules become faster, which does not match, in fact is opposite to the observational results). On the contrary if discarding our previous conclusion that $b = 1$ we think that we may vary b as a parameter and may obtain C_3 for each b following Eq. (11), the problem in doing so is that C_3 cannot vary with b because the former depends upon the composition of the bead with a small possible variation due to temperature and pH factor as discussed earlier, while the latter depends upon the kinetics of the growth and is a constant of the process and must remain unchanged for all the hydro-gel beads of identical compositions. So we cannot vary b as a parameter at all. It must have a constant value like a and that value must be unity.

Again, since the polymer contains a fixed number of molecules within a given volume in solid phase, the number of sites N that can store exactly one absorbed water molecule should also be constant. This number may be assumed to be directly proportional to the number of molecules (N') in each bead. Hence (for some dimensionless constant C_4)

$$N = C_4 N' = C_4 \frac{v\rho}{\bar{m}} \quad (12)$$

where ρ is the density of the dry bead (both v and ρ must be measured in c.g.s. system of units) while $\bar{m}$ is the mass of a single hydro-gel molecule (or a single polymer unit probably acryl amide and in fact $\bar{m} = 1.2 \times 10^{-22}$ g) of the given material. Hence

$$\frac{v}{V_{\max}} = \frac{1}{1 + C_4 \frac{w\rho}{\bar{m}}} = k \quad (13)$$

which appears to be a constant. Alternatively one may think that the number of active sites per unit volume of dry hydro-gel is the same for all the beads of same color. This number is expected to be proportional to the initial volume of a bead, *i.e.* αv , α being the constant of proportionality. According to our assumption each active site may attach only a single water molecule hence the increase in volume of the bead may be expressed as

$$V_{\max} - v = \alpha v w \quad (14)$$

yielding

$$\frac{v}{V_{\max}} = k = \frac{1}{1 + \alpha w} \quad (15)$$

implying $\alpha = N/v$. From our experimental observations and proposed theoretical model we may estimate the other constants and parameters (some we have done already) a , w , α , ρ , N , f *etc.* keeping in mind that the net increase in volume of each bead (w) is due to the absorption of water molecules (each having a volume u) only and hence it must be proportional to the entire volume of the water molecules absorbed in the process. Let the corresponding constant of proportionality be λ . Hence

$$w = \lambda u = 3 \times 10^{-23} \lambda \text{ cm}^3 \quad (16)$$

Also the number of water molecules absorbed in the process may be obtained from the relation

$$N = \frac{V_{\max} - v}{\lambda u} \quad (17)$$

In another study we may establish that the value of a is a negative half integral number in the following manner. Analysis of Eqs. (10) or (11) evaluates the dimension of C_3 to be $L^{-2a} T^{-1}$ which restricts us in choosing any arbitrary value of a , because it will create difficulty in understanding the physical property of the constant C_3 . Also a must take only those values such that the power of L in the dimension of C_3 must become integer (to avoid any fractal nature). This may be achieved if we assume some integral or half-integral values of a . We also have some strong arguments about the signs of a , which happens to be negative. The nature of the experimental plots supports this fact. The slopes of positive a , b plots increase first and then decrease (sigmoidal) which does not seem to be the case we observe with our experimental data-set; while the slopes of the curves for negative a and positive b should always decrease starting from the initiation of the process, the fact clearly seen in the experimental plots (Fig. 1). We are thus searching a negative and half-integral a , which eventually being the first of that kind namely $a = -1/2$. Following two arguments will strengthen our conclusion.

The direct integration of Eq. (9) without any approximation, with $a = -1/2$ and $b = 1$ yields

$$\begin{aligned} & (v^{\frac{1}{3}} - V(t)^{\frac{1}{3}}) + \frac{V_{\max}^{\frac{1}{3}}}{3} \ln \left(\frac{V_{\max}^{\frac{1}{3}} - v^{\frac{1}{3}}}{V_{\max}^{\frac{1}{3}} - V(t)^{\frac{1}{3}}} \right) + \frac{V_{\max}^{\frac{1}{3}}}{6} \ln \left(\frac{V_{\max}^{\frac{2}{3}} + V(t)^{\frac{1}{3}} V_{\max}^{\frac{1}{3}} + V(t)^{\frac{1}{3}}}{V_{\max}^{\frac{2}{3}} + v^{\frac{1}{3}} V_{\max}^{\frac{1}{3}} + v^{\frac{2}{3}}} \right) + \\ & \frac{V_{\max}^{\frac{1}{3}}}{\sqrt{3}} \left[\operatorname{atan} \left(\frac{V_{\max}^{\frac{1}{3}} + 2V(t)^{\frac{1}{3}}}{\sqrt{3} V_{\max}^{\frac{1}{3}}} \right) - \operatorname{atan} \left(\frac{V_{\max}^{\frac{1}{3}} + 2v^{\frac{1}{3}}}{\sqrt{3} V_{\max}^{\frac{1}{3}}} \right) \right] = \left(\frac{C_3}{3} \right) t \end{aligned} \quad (18)$$

Fitting this equation to the normalized $V-t$ data set (using curve-fitting technique in MATLAB) for all the five beads and keeping in mind that $V'_{\max} = fV_{\max}$ one may obtain a figure identical to Fig. 1 and finally may determine the unknown parameters f and C_3 as the output.

Inspection of those output parameters reveals that only for the largest bead the fitting parameters yield good agreement (f value tends towards unity). Hence assuming only the result for the bead 5 to be correct we may determine the constant k (following Eq. (15)) and the f values for other beads using the data reported in Table 1.

Following Eqs. (11) and (18) we now achieve respectively

$$C_3 = \frac{V'_{\max} \frac{1}{f^{\frac{1}{3}} T_{\exp}}}{\sum_{p=0}^{\infty} \left[\frac{\left(f^{p+\frac{4}{3}} - (k)^{p+\frac{4}{3}} \right)}{\left(p + \frac{4}{3} \right)} \right]} \quad (19)$$

$$C_3 = \frac{V'_{\max} \frac{1}{f^{\frac{1}{3}} T_{\exp}}}{\left[\begin{aligned} & 3(k^{\frac{1}{3}} - f^{\frac{1}{3}}) + \ln \left(\frac{1 - k^{\frac{1}{3}}}{1 - f^{\frac{1}{3}}} \right) + \frac{1}{2} \ln \left(\frac{1 + f^{\frac{1}{3}} + f^{\frac{2}{3}}}{1 + k^{\frac{1}{3}} + k^{\frac{2}{3}}} \right) + \\ & \sqrt{3} \left(\operatorname{atan} \left(\frac{1 + 2f^{\frac{1}{3}}}{\sqrt{3}} \right) - \operatorname{atan} \left(\frac{1 + 2k^{\frac{1}{3}}}{\sqrt{3}} \right) \right) \end{aligned} \right]} \quad (20)$$

In the theoretical limit ($f \rightarrow 1$, $k \rightarrow 0$, $T_{\exp} \rightarrow T_{\text{theo}}$, which tends towards infinity) Eq. (19) becomes

$$C_3 = \frac{V'_{\max} \frac{1}{T_{\text{theo}}}}{\sum_{p=0}^{\infty} \frac{1}{p + \frac{4}{3}}} = \frac{V'_{\max} \frac{1}{T_{\text{theo}}}}{\zeta \left(1, \frac{4}{3} \right) + 0.75} \quad (21)$$

where $\zeta(1, a)$ is the generalized Riemann-zeta function^[22]. And we know that the series diverges for $l = 1$ which clearly establishes our earlier assumption (consequences of Eq. (10) and fixing the value of b to 1). On the other hand the series summation $\sum_{p=0}^{\infty} \frac{k^{p+a}}{p+a}$ at some positive a and $0 < k < 1$ is convergent which once again confirms

our previous assumption. Similar conclusions may also be derived from Eq. (20). Hence with the suitable choice of f , C_3 may be estimated as done below in Table 2.

Table 2. Evaluation of some typical parameters with $k = 0.0186$, $C_3 = 0.4729 \text{ cm} \cdot \text{h}^{-1}$
(using bead 5 data-fitting and the relation $V'_{\max} = fV_{\max}$)

Bead No.	$\frac{v}{V'_{\max}}$	f	N (using Eq. (17)) $\times 10^{25}/\lambda$	C_3 (using Eq. (19)) ($\text{cm} \cdot \text{h}^{-1}$)	C_3 (using Eq. (20)) ($\text{cm} \cdot \text{h}^{-1}$)	C_3 (fitting Eq. (18) to data) ($\text{cm} \cdot \text{h}^{-1}$)
5	0.0202	0.9223	5.8994	0.4326	0.4326	0.4729
4	0.0201	0.9254	2.0036	0.6488	0.6488	0.4962
3	0.0192	0.9688	1.1281	0.8586	0.8586	0.8076
2	0.0198	0.9394	0.7390	0.7232	0.7232	0.6759
1	0.0206	0.9029	0.4521	0.6604	0.6604	0.5684

In our earlier discussion we have demanded C_3 to be constant (according to our earlier assumption it is associated with only the chemical properties of the hydro-gel). But while computing it using a different method we observe that it is actually of short-range varying nature and in fact varies with the initial size of the PAA beads. The value of C_3 initially increases with the size of the beads and reaches certain maximum and then decreases with further increase in the size of the beads. Also the computed values of C_3 , tabulated in last three columns of Table 2 almost agree with each other making our entire theory more consistent.

We may also estimate C_3 using a physical definition of it. In order to define C_3 we introduce a new term virtual thickness which may be defined as $\tau(t) = R_{\max} - R(t)$. At a certain instant it is the deficit of the present thickness from the maximum thickness. The corresponding volume deficit from the maximum may be termed as the virtual volume of the bead. At any instant the fractional change in the virtual volume of the bead per unit

time (f_t) is inversely proportional to the radius of the bead at that instant and the corresponding proportionality constant is C_5 (where $C_5 = (4\pi/3)^{-1/3}C_3$), in other words

$$f_t = \frac{\Delta V(t)/(V_{\max} - V(t))}{\Delta t} = \frac{C_5}{R(t)} \quad (22)$$

which eventually leads to

$$C_3 \approx \left(\frac{4\pi}{3}\right)^{\frac{1}{3}} \left[\frac{D(t)}{2\Delta t} \right] \left[\frac{D^3(t+\Delta t) - D^3(t)}{D_{\max}^3 - D^3(t)} \right] \quad (23)$$

We take some typical data sets below in Table 3 (units of t is h and those for the radius and volume are cm and mL respectively) to evaluate C_3 following Eq. (23).

Table 3. Numerical evaluation of C_3 following Eq. (23) and Table 1

Bead No.	Data set 1	Data set 2	Data set 3	Data set 4	Data set 5
	$t = 0$	$t = 1.0$	$t = 0.5$	$t = 3.0$	$t = 2.0$
5 ($D_{\max} = 1.5102$)	$\Delta t = 1.0$ $C_3 = 0.1209$	$\Delta t = 2.0$ $C_3 = 0.2484$	$\Delta t = 1.0$ $C_3 = 0.2971$	$\Delta t = 3.0$ $C_3 = 0.2600$	$\Delta t = 0.5$ $C_3 = 0.5399$
4 ($D_{\max} = 1.0570$)	$t = 0$ $\Delta t = 1.0$ $C_3 = 0.0909$	$t = 1.0$ $\Delta t = 2.0$ $C_3 = 0.2752$	$t = 0.5$ $\Delta t = 1.0$ $C_3 = 0.3284$	$t = 3.0$ $\Delta t = 0.5$ $C_3 = 0.6050$	$t = 2.0$ $\Delta t = 0.5$ $C_3 = 0.5453$
3 ($D_{\max} = 0.8691$)	$t = 0$ $\Delta t = 1.0$ $C_3 = 0.1178$	$t = 1.0$ $\Delta t = 1.0$ $C_3 = 0.4954$	$t = 0.5$ $\Delta t = 1.0$ $C_3 = 0.4077$	$t = 1.5$ $\Delta t = 0.5$ $C_3 = 0.6690$	$t = 2.0$ $\Delta t = 0.5$ $C_3 = 0.7098$
2 ($D_{\max} = 0.7556$)	$t = 0$ $\Delta t = 1.0$ $C_3 = 0.1220$	$t = 1.0$ $\Delta t = 1.0$ $C_3 = 0.5047$	$t = 0.5$ $\Delta t = 1.0$ $C_3 = 0.4248$	$t = 1.0$ $\Delta t = 0.5$ $C_3 = 0.8293$	$t = 0$ $\Delta t = 0.5$ $C_3 = 0.1584$
1 ($D_{\max} = 0.6415$)	$t = 0$ $\Delta t = 1.0$ $C_3 = 0.1234$	$t = 1.0$ $\Delta t = 0.5$ $C_3 = 0.9275$	$t = 0.5$ $\Delta t = 1.0$ $C_3 = 0.4203$	$t = 0$ $\Delta t = 1.5$ $C_3 = 0.0907$	$t = 0.5$ $\Delta t = 0.5$ $C_3 = 0.6639$

From the above Table 3 it is clear to us that as t becomes sufficiently greater than Δt , the computed value of C_3 becomes more nearer to its tabulated value in Table 2 which is quite understandable.

Let us now estimate λ from a direct measurement of decrease in volume of the water content in a volumetric cylinder due to swelling of the beads immersed into the water in the same cylinder (again using normalization on large number of identical beads while calculating the gross volume decrease in the water content of the cylinder, explained in details in the method part)

$$\lambda = \frac{\text{maximum increase in volume of a crystal bead due to swelling}}{\text{volume of water absorbed by that bead}} \quad (24)$$

To determine the density (ρ) of the dry PAA we again use some normalization technique. We have taken the ratio of the total mass of a large number of transparent beads under dry condition to their total initial volume (we have grouped the data in sets, each of a specific size) to obtain

$$m = v\rho \quad (25)$$

We may also notice the following relations (where m_w is the mass of a single water molecule.)

$$V_{\max} - v = \lambda Nu = \lambda(\text{volume of water absorbed}) = \frac{\lambda u}{m_w}(M_{\max} - m) \quad (26)$$

$$N = \frac{\text{max. increase in mass of a dry crystal bead due to swelling}}{\text{mass of a single water molecule}} = \frac{M_{\max} - m}{3 \times 10^{-23} \text{ g}} \quad (27)$$

$$\lambda u(M_{\max} - M'_{\max}) = m_w (V_{\max} - V'_{\max}) \quad (28)$$

In Table 4 below we have estimated some constants for bead 5 using the data reported in Table 1 and Table 2 and with the helps of Eqs. (24)–(28).

Table 4. Evaluation of some parameters for bead 5 (using normalized data taken from identical set of beads)

ρ (g·cm ⁻³)	m (g)	λ	$M_{\max}$ (g)	$M'_{\max}$ (g)	$N \times 10^{-25}$	$C_4 = \frac{N\bar{m}}{\rho}$	$\alpha = N/V \times 10^{-27}$
3.04	0.102	0.672	2.736	2.527	8.779	3465.4	2.621

In Table 4 the fact $\lambda < 1$ implies that the increase in volume of the PAA's is less than the volume of water absorbed by them indicating a porous nature of hydro-gel beads. From micrographs of highly porous hydro-gels, provided by various groups of researchers^[23, 24], it is often found that almost the entire surface area of hydro-gel is covered with pores^[25–28] which clearly resembles with our present model. The total number of molecules inside the bead may be computed as the ratio $m/\bar{m} = 8.50 \times 10^{20}$. Hence the number of sites storing a single water molecule may be considerably higher than the total number of molecules in the bead. But not all these available sites will directly take part in the diffusion process. The sites at the uppermost layer of the bead are the ones responsible for the diffusion of water into PAA.

We may define the weight swelling ratio (q) in our model in the following manner (in consistent with its definition given in the introduction)

$$q(t) = \frac{\text{increase in vol. of a crystal bead at time } t}{\text{average increase in vol. due to the absorption of a single water molecule}} \times \frac{\text{weight of a water molecule}}{\text{weight of dry crystal}} = 3 \times 10^{-23} \left(\frac{V(t) - v}{wv\rho} \right) \quad (29)$$

As stated earlier, in Figs. 2(a) and 2(b) we have plotted $t/q(t)$ against t and $\ln[q(t) + 1]$ against $\ln t$ (where t is in h.) respectively^[5, 6]. From the data associated with these plots we may now estimate A and B (the reciprocals of the initial and maximum swelling rates respectively) and K, s (the swelling constant and exponent respectively in dimensionless format) defined earlier again using some curve fitting technique in MATLAB. We have presented the estimates of those parameters in Table 5 which are found to be consistent with the earlier experimental observations^[15].

The value of s (< 0.5) indicates that the diffusion process particular to our experiment is Fikian by nature.

Table 5. Evaluations of A, B, K, s through curve-fitting

Bead No.	A	B (h ⁻¹)	s	K
1	9.2487	0.1256	0.4652	0.6751
2	18.7134	0.1964	0.4110	0.5464
3	26.0794	0.1762	0.4393	0.4354
4	40.1471	0.1610	0.4462	0.3587
5	64.5476	0.2006	0.3911	0.3678

CONCLUSIONS

In our analysis we have estimated all the constants of our process (from C_1 to C_5), thereby proposing a new model that governs the growth mechanism of a spherical hydro-gel bead. Also we have analyzed various swelling properties, determining the initial and maximum swelling rates, the swelling constants and exponents *etc.* The variation of volume and swelling parameters with time has also been analyzed using suitable curve-fitting methods. Our theoretical models are in very good agreement with our experimental findings. We

have recently performed some other relevant works on hydro-gel swelling both in water as well as in sugar solution. In summary our present analysis shows some interesting results listed below:

- (1) New dynamical model based on Eqs. (7) and (9) excludes any requirement of mass-time data and uses volume as the only dynamical variable as a function of time.
- (2) The ratio of the dry to maximum swollen volume of hydro-gel beads remains constant.
- (3) The relation $(V_{\max})^{-1/3} T_{\text{theo}} = \text{constant}$, has been established for hydro-gels.
- (4) With a computation of the parameter λ we have shown that the increase in volume of hydro-gels is less than the volume of water absorbed, supporting the porous nature of the material.
- (5) Number of active sites per unit volume of the hydro-gel (α) may be computed from our model.
- (6) The converging property of a mathematical series is successfully utilized to study the natural growth process (see Eq. (21) and the relevant discussions) of hydro-gels.
- (7) The reason for the decrease in growth rate with the increase in surface area of the hydro-gel beads may be explained.
- (8) That the diffusion process studied by us is Fickian has been clearly established.

REFERENCES

- 1 Pal, K., Banthia, A.K. and Majumdar, D., *Dsgnd. Monom. Polym.*, 2009, 12: 197
- 2 Ganji, F., Vasheghani-Farahani, S. and Vasheghani-Farahani, E., *Iranian Polym. J.*, 2010, 19(5): 375
- 3 Thakur, A., Wanchoo, R.K. and Singh, P., *Chem. Biochem. Eng. Q*, 2011, 25(2): 181
- 4 Flory, P.J. and Rehner, B.D., *J. Chem. Phys.*, 1943, 11: 512
- 5 Hoffman, A.S., *Adv. Drug Delv. Rev.*, 2002, 54: 3
- 6 Martinez-Ruvalcaba, A., Sanchez-Diaz, J.C., Becerra, F., Cruz-Barba, L.E. and Gonzalez-Alvarez, A., *eXPRESS Polym. Lett.*, 2009, 3(1): 25
- 7 Reeves, R., Ribeiro, A., Lombardo, L., Boyer, R. and Leach, J.B., *Polymer*, 2010, 2: 252
- 8 Caykara, T., Kiper, S. and Demirel, G., *Eur. Polym. J.*, 2006, 42: 348
- 9 Porter, T.L., *Sensors*, 2007, 7: 1980
- 10 Moon, J.R., Kim, B.S. and Kim, J.H., *Bull. Kor. Chem. Soc.*, 2006, 27: 981
- 11 Min, S.K., Kim, S.H. and Kim, J.H., *J. Ind. Eng. Chem.*, 2000, 6: 276
- 12 Kunioka, M., *Macromol. Biosci.*, 2004, 4: 324
- 13 Alaei, J., Boroojerdi, S.H. and Rabiei, Z., *Petroleum & Coal.*, 2005, 47: 32
- 14 Peng, H.T., Martineau, L. and Shek, P.N., *J. Matter Sci: Mater Med.*, 2007, 18: 975
- 15 Karadag, E., Saraydin, D. and Guven, O., *Nucl. Instr. and Meth. In Phys. Res. B*, 2004, 225: 489
- 16 Smoluchowski, M.V., *Ann. Phys.*, 1915, 353 (4. Folge 48): 1103
- 17 Langevin, P., *C. R. Acad. Sci. (Paris)*, 1908, 146: 530
- 18 Roy, S., Majumdar, P. and Ghosh, S., *Natural Sci.*, 2011, 3(9): 802
- 19 West, G.B., Brown, J.H. and Enquist, B.J., *Science*, 1997, 276: 122
- 20 West, G.B., Brown, J.H. and Enquist, B.J., *Nature*, 1999, 400: 664
- 21 Gupta, B.D., "Mathematical physics", 2nd Rvds. Edn., Vikash Publishing House Pvt. Ltd., New Delhi, 2003, p. 5
- 22 Gupta, B.D., "Mathematical physics", 2nd Rvds. Edn., Vikash Publishing House Pvt. Ltd., New Delhi, 2003, p. 120
- 23 Dinu, M., Perju, M.M., Cazacu, M. and Dragan, E.S., *Cellulose Chem. Technol.*, 2011, 45: 197
- 24 Gemeinhart, R.A., Park, H. and Park, K., *Polym. Adv. Technol.*, 2000, 11: 617
- 25 Das, P., Biswas, D., Roy, S. and Majumdar, P., *Int. J. Drug Delv.*, 2012, 4: 20
- 26 Roy, S. and Majumdar, P., *Int. J. Drug Dev. Rsch.*, 2013, 5: 99
- 27 Roy, S. and Majumdar, P., *Int. J. Drug Dev. Rsch.*, 2013, 5(1): 252
- 28 Majumdar, P., *World J. Mod. Sim.*, 2013, 9: 269