



Temperature effect on swelling properties of commercial polyacrylic acid hydrogel beads.

Dr. Ahmed. M. Saeed.

Dept. of Chemistry, College of Science, University of Wasit, Wasit, Iraq.

ABSTRACT

Due to the fact that many application processes take place at different temperature, better examining and understanding of swelling properties as a function of temperature is essential for such application. The temperature effect on the swelling properties of commercial polyacrylic acid (PAA) hydrogel beads was investigated as a function of time and temperature. Gel bead size, swelling equilibrium capacity, diameter, weight, water retention, swelling ratio, welling degree and fractional hydration were studied to investigate the swelling properties of hydrogel bead at a given temperature. Diffusion type and its related parameters were studied and calculated. The kinetic model was applied on experimental data using second order model, the kinetic parameters were calculated. The maximum swelling ratio was calculated as 233.7 at 40 °C. In experiment of the swelling non- Fickian diffusion was found.

Key word: Swelling properties, temperature effect, polyacrylic acid, commercial hydrogel.

1. INTRODUCTION

Hydrogels are three-dimensional networks of hydrophilic polymer chain in between liquid and solid [1, 2]. One of the most interesting features is their capability to swell and shrink, depending on their surroundings [3, 4]. Hydrogels are cross- linked macromolecules with segment of hydrophilic groups. The cross linking agent, a monomer with two or more double bonds, provides the polymer network structure by connecting the long, linear chains in these polymerization. Cross linking the polymer chain form a three- dimensional elastic polymer network [5, 6]. When such a network is in contact with water or an aqueous solution, it increases its volume by absorbing water and solutes. The process called swelling [7, 8]. Polymeric gels (hydrogels) are the objects of intensive studies. The ability to absorb and store much water and water solution makes hydrogels unique materials for a variety application [9 - 13]. Hydrogel networks formed from polyacrylic acid (PAA) have the ability to absorb more than (5-10) hundred times their weight in water and they are considered as the basis of a class of materials called super absorbents [14]. Super absorbent polymers (SAP_s) are compounds that absorb water and swell into many times their original size and weight. The network can swell in water and hold a large amount of water while maintaining the physical dimension structure. SAP_s are widely used in personal hygiene products [16]. Resent researches are focused in application area of SAP_s, e.g. ion exchange resins, membranes for hemodialysis [17,18], biosensing, soft actuators/ valves, catalysis, concentration of viruses, vitamin, bovine serum albumin and controlled drug delivery [21]. SAP_s or hydrogels have been also studied for the concentration of macromolecules [22]. Hydrogel were evaluated for their use as fertilizer with the immobilization of the olive mill wastewater [23]. Due to the fact that many application processes take place at different temperature, better examining and understanding of swelling properties as a function of temperature is essential for such application. Thus, the aim of this study is the determination of the temperature effect on swelling parameters of a commercially available polyacrylic hydrogel

beads. Different swelling parameters were studied and calculated. The type of diffusion and diffusion kinetic were also in our consideration in this study.

2. Experimental

2.1. Materials

Distilled water, Hydrochloric acid (HCl) supplied from BDH and commercially available hydrogel beads which are early identification as polyacrylic acid (PAA) [24] were used.

2.2. Instrumentation

Electrical oven cabinet type (JEIO TECH, Korea) was used throughout this study. Ametrohm E.632 pH meter (Switzerland) with glass combination electrode was used for solution pH measuring. Vernier caliper with 0.01 mm measuring accuracy was used for measurement of the diameter of the gel beads. Sartorius BL 210 S (Germany), max. 210 g, D 0.1 mg, was used for gel beads weighing.

2.3. Batch experiment

Equilibrium swelling experiments were used to investigate the swelling properties of the commercially available hydrogel beads, through a batch process. A series of plastic containers each one contain a 50 mL of distilled water with pH of 6.3. The hydrogel beads with 0.0346 g weight and 3.56 mm diameter were placed in each container, and left for contact time range of 1-12 hr. at a temperature range of 10 – 40 °C. The weight of absorbed water (W_{H_2O}) was calculated by using of the following equation:

$$W_{H_2O} = (W_s - W_o) \dots\dots\dots 1$$

Where W_s , W_o are the weight of swollen bead at t time (Fig. 1), and the initial weight of gel bead (0.0346 g) respectively. While the volume of the swollen bead at any time or at equilibrium was calculated by using the following equation [25]:

$$V = \frac{4}{3} \pi (r_i - r_o)^3 \dots\dots\dots 2$$

Where r_i , r_o are a radius of the hydrogel bead at t time and the initial radius (1.78 mm). The water volume penetrated into hydrogel bead was calculated by the difference between initial and equilibrium (or at t time) volume. All of the experimental results were the average of triplicate experiments.

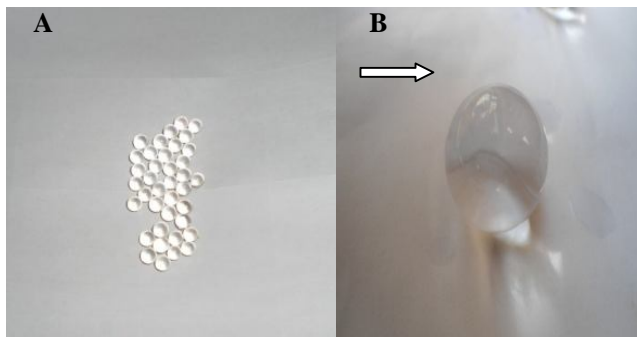


Figure 1. The profile and size of gel bead before (A) and after (B) swelling.

3. Results and discussion

3.1. Temperature influence on weight and size of swollen hydrogel beads.

Temperature influence on weight and size of swollen hydrogel beads was investigated as a function of time and temperature. The results obtained (Table 1 and 2) indicated that the weight, diameter and size of hydrogel bead are affected strongly with temperature variation.

Table.1. Results of hydrogel bead diameter (D_i) mm at different time and temperature.

Time (hr)	Temperature °C			
	10 °C	20 °C	30 °C	40 °C
1	8.50	10.50	11.68	13.70
2	10.30	13.00	16.36	18.10
4	13.40	16.50	18.56	21.70
6	16.20	18.50	20.12	23.60
8	17.80	19.60	22.02	25.24
10	19.50	20.80	23.04	25.32
12	20.50	22.00	24.00	25.34

Table.2. Results of hydrogel bead weight (W_i) g at different time and temperature.

Time (hr)	Temperature °C			
	10 °C	20 °C	30 °C	40 °C
1	1.072	1.310	1.810	2.490
2	1.305	2.980	3.760	4.280
4	2.512	3.680	4.510	5.900
6	3.613	4.390	5.290	6.760
8	4.298	5.190	6.030	7.990
10	5.120	5.570	6.320	8.100
12	5.400	5.980	6.810	8.120

The values of studied parameters (e.g. diameter, weight, bead volume, water volume and other related parameters W_{H_2O} / W_o and V_{H_2O} / V_o), were small at lower value of temperature (10, 20 °C), especially at the beginning of swelling process. That may be due to the small values of the internal energy and entropy, which were lead to low degree of movement and small diffusion of solution into internal hydrogel bead structure, that mean a small quantity of water penetrate into hydrogel bead and small variation in weight, diameter and other parameters (Table.3, 4). Figure 2, 3, 4 and 5 shown the relation between time, temperature, weight, diameter, and (weight and volume) of penetrated water. While at high temperature a sharp increase in diameter and weight was take place, that may be due to the increasing in the entropy and internal energy as well as the temperature increased, which was lead to increase the diffusion of solution and finally lead to increase the penetrated water quantity, that causes the increase in value of diameter, weight, water weight and water volume as shown in Table 3 and 4.

Table.3. Results of W_{H_2O} (g) at different time and temperature.

Time (hr)	Temperature °C			
	10 °C	20 °C	30 °C	40 °C
1	1.037	1.275	1.775	2.455
2	1.270	2.945	3.725	4.245
4	2.477	3.645	4.475	5.865
6	3.578	4.355	5.255	6.725
8	4.263	5.155	5.995	7.955
10	5.085	5.535	6.285	8.065
12	5.365	5.945	6.775	8.085

Table.4. Results of swelling water volume (cm³) at different time and temperature.

Time hr.	Temperature °C			
	10 °C	20 °C	30 °C	40 °C
1	0.063	0.175	0.280	0.550
2	0.160	0.441	1.100	1.610
4	0.499	1.135	1.610	3.130
6	0.749	1.746	2.460	4.220
8	1.512	2.161	3.290	5.340
10	2.121	2.684	3.870	5.400
12	2.546	3.284	4.470	5.400

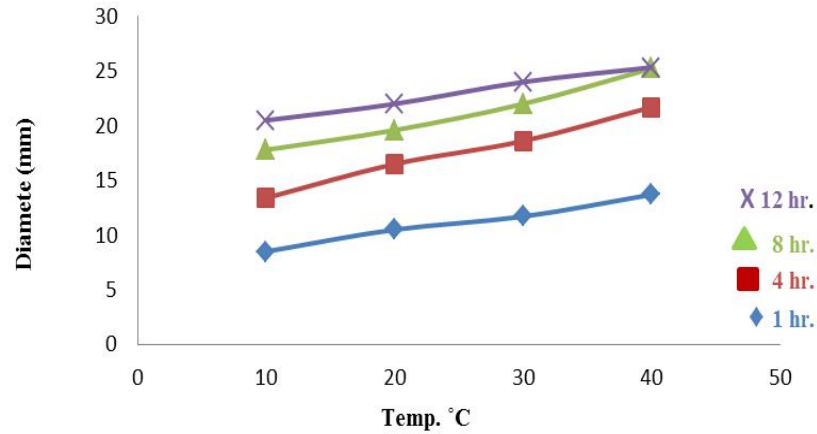


Figure 2. Relationship between temperature and diameter .

Other parameters which are related to water volume and water weight (e.g. W_{H_2O} / W_o and V_{H_2O} / V_o) were calculated and listed in Table 5 and 6. The results revealed that there is a clear proportional relationship between temperature and ratio of W_{H_2O} / W_o and V_{H_2O} / V_o , which were increase with temperature increasing until reach constant weight and volume at equilibrium after 12 hr at 40 °C as shown in Fig. 6 and Fig. 7.

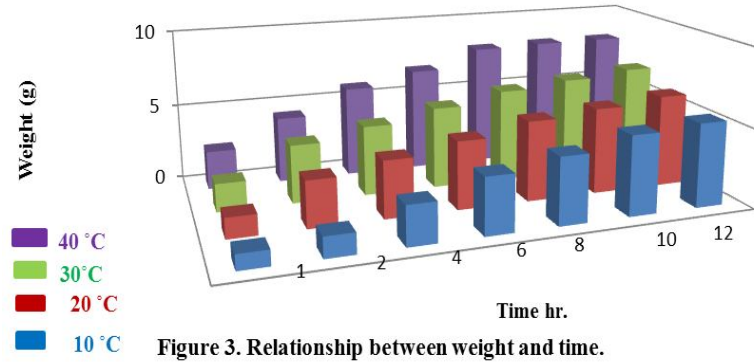


Figure 3. Relationship between weight and time.

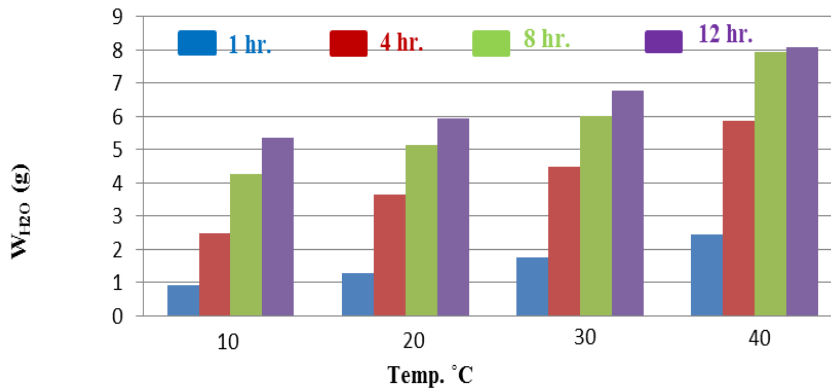


Figure 4. Relationship between water weight and temperature.

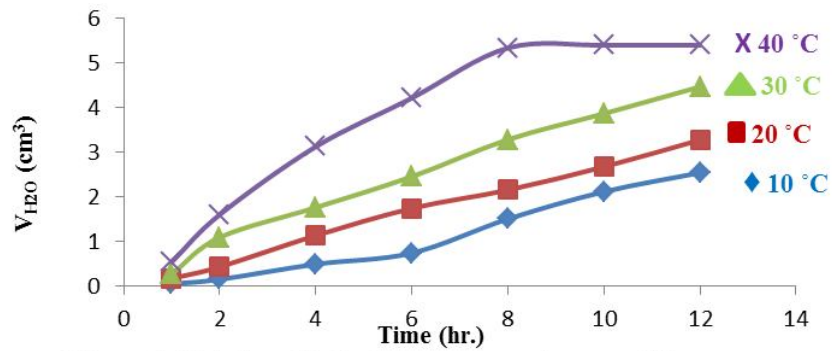


Figure 5. Relationship between water volume and time.

Table.5 . results of W_i / W_o at different time and temperature.

Time (hr)	Temperature °C			
	10 °C	20 °C	30 °C	40 °C
1	29.98	37.86	52.31	71.97
2	37.72	86.12	108.67	123.70
4	72.60	106.35	130.35	169.52
6	104.42	126.88	152.89	195.37
8	124.22	150.00	174.28	230.92
10	147.98	160.98	182.66	234.10
12	156.07	172.83	196.82	234.68

Table.6 . Results of V_{H_2O} / V_O at different time and temperature.

Time (hr)	Temperature °C			
	10 °C	20 °C	30 °C	40 °C
1	2.67	7.42	11.86	23.31
2	6.78	18.68	46.61	68.22
4	21.14	48.09	68.00	132.63
6	31.74	73.98	95.76	178.81
8	64.07	91.57	139.41	226.27
10	89.87	113.73	163.98	228.81
12	107.88	139.15	189.41	228.81

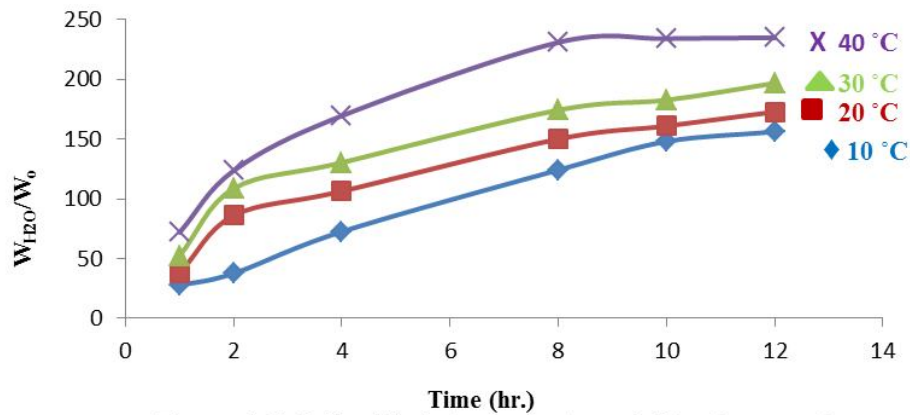


Figure 6. Relationship between water weight ratio vs time.

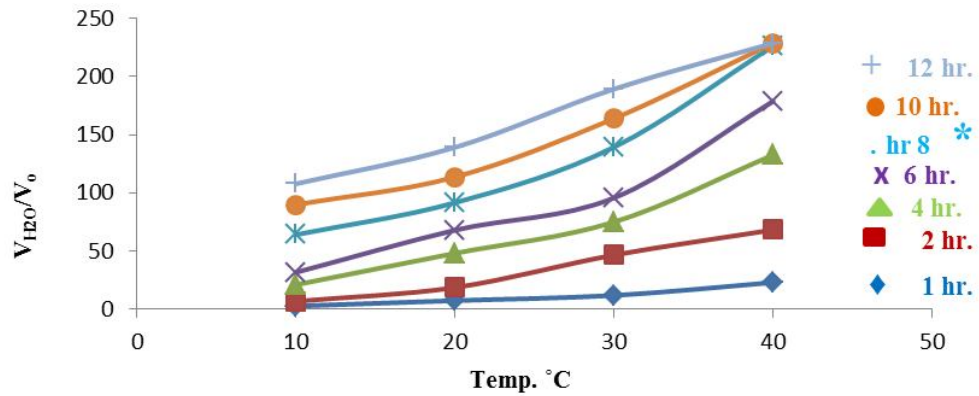


Figure 7. Relationship between water volume ratio versus temperature.

3.2. Determination of swelling degree

The swelling ratio (SR) and swelling degree (SD) or swelling percentage (S %) of hydrogel bead was calculated according to the following equations:

$$SR = W_i / W_o \dots\dots\dots 3$$

$$SD (S \%) = SR \times 100 \dots\dots\dots 4$$

Where W_i , W_o are the weight of swollen hydrogel bead at equilibrium or at t time and initial weight of hydrogel bead respectively. The results obtained are listed in Table 7, which was revealed that the value of SD was small at the beginning of swelling process especially in the low temperature (10, 20 °C), while at high temperature a significant increase in SD value was observed and the swelling process reach the equilibrium at a time beginning from 6 – 12 hr with a temperature of 40 °C. That may be due to the large quantity of water which was penetrated into internal structure of hydrogel bead as a result of increase the entropy of solution, which lead to increase the diffusion process as shown in Fig. 8 and 9.

Table. 7 . Results of water swelling ratio at different time and temperature.

Time hr.	Temperature °C			
	10 °C	20 °C	30 °C	40 °C
1	30.99	36.86	51.31	70.97
2	36.72	85.12	107.67	122.70
4	71.60	112.58	129.35	169.52
6	103.42	125.88	151.89	194.60
8	123.22	149.00	173.28	229.92
10	146.98	159.98	181.66	233.10
12	154.78	171.83	195.82	233.70

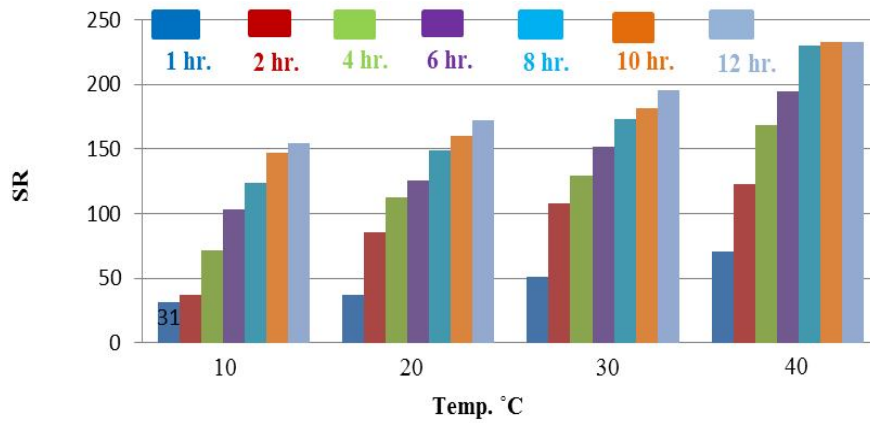


Figure 8. Relationship between SR versus temperature.

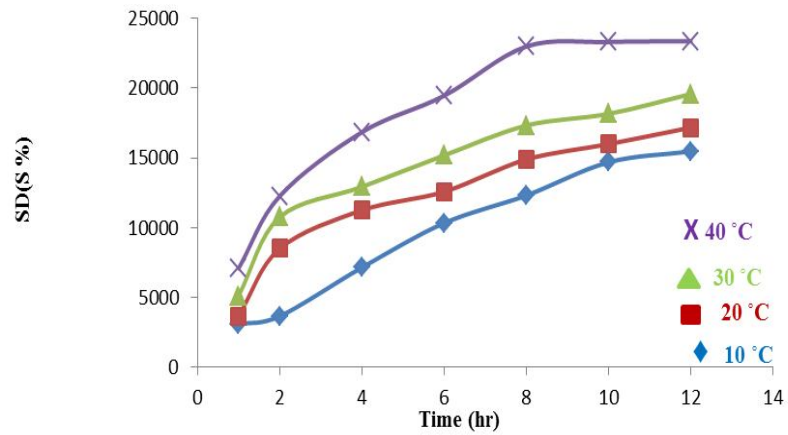


Figure 9. Relationship between SD (S%) versus time.

3.3. Diffusion study

The nature of diffusion of water into hydrogel bead was determined by using the following equation [26]:

$$F = k t^n \dots\dots\dots 5$$

Where F is the fractional hydrate uptake at t time, k is a constant incorporating characteristics of macromolecular polymer system and the penetrate solution, and n is the diffusion exponent, which is indicative of the transport mechanism. n and k can be obtained from the slopes and intercepts of ln F vs. ln t plots (Fig.10). Equation 5 is valid for the first 60% of the fractional uptake.

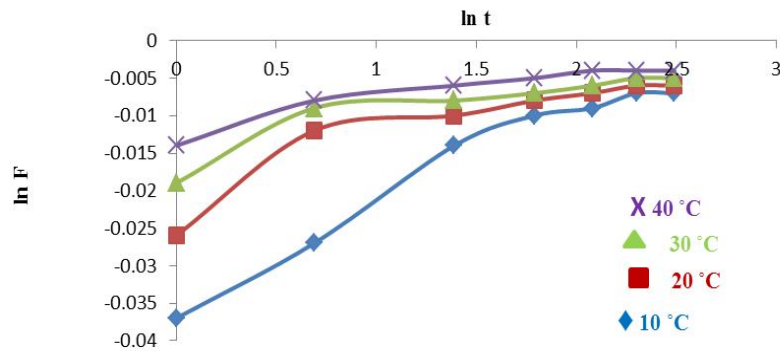


Figure 10. Relationship between ln F versus ln t.

The results obtained are tabulated in Table 8, which is revealed that the diffusion behavior of water into hydrogel bead is found to have Fickian character, due to the value of n is less than 0.5[27].

Table.8. Some swelling parameter of hydrogel bead at different temperature.

Temp. °C	*S _{eq} %	n	k x 10 ⁻²	K _{0.5}
10	15478	0.013	3.510	
20	17183	0.007	2.160	194.2
30	19582	0.005	1.590	1641.6
40	23370	0.004	1.220	2289

*S_{eq}% represent swelling degree (SD) = SR x 100

3.4. Swelling rate coefficients

Swelling characteristic particularly the rate of aqueous swelling of water uptake was followed by some methods. Fig. 11 shows the equilibrium swelling degree (S%) for the hydrogel versus the square root of contact time for the first 60 % of the fractional uptake. Excellent linear correlations were observed. Linear slopes of all degree of temperature in Fig. 11 were assumed to represent relative swelling rate coefficients (K_{0.5}), the obtained results are tabulated in Table 8.

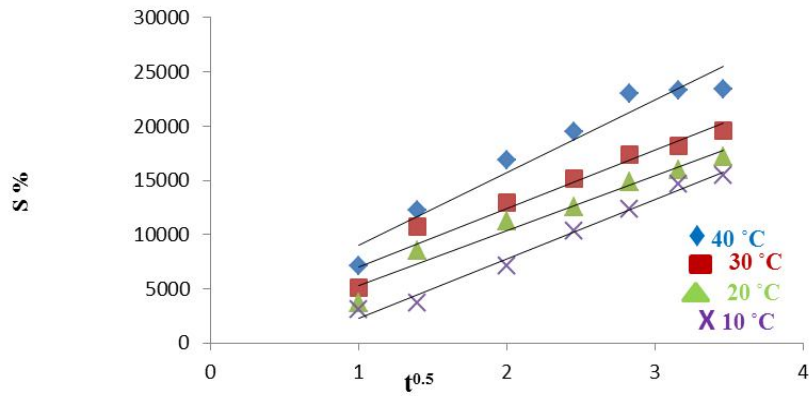


Figure 11. Relationship between S% versus $t^{0.5}$.

The results in Table 8 revealed that the swelling process of the solution which has a temperature degree of 40 °C was faster than the other temperature due to the highest $K_{0.5}$ value of 2289 [28].

3.5. Fractional hydration and water retention

The following equations were used to estimated the fractional hydration (FH) and water retention (W_{RT}) values as a function of temperature and time [29, 30].

$$W_{RT} = (W_t - W_d) / (W_s - W_d) \dots\dots\dots 6$$

$$FH = (W_t - W_o) / W_t \dots\dots\dots 7$$

Where W_d , W_o are the weight of the dried hydrogel bead, W_s is the weight of the swollen hydrogel at largest time, and W_t is the weight of swelled hydrogel bead at t time.

Table.9.Results of water retention capacity (W_{RT}) at different time and temperature.

Time (hr)	Temperature °C			
	10 °C	20 °C	30 °C	40 °C
1	0.114	0.158	0.220	0.304
2	0.157	0.364	0.461	0.525
4	0.306	0.438	0.541	0.725
6	0.443	0.539	0.650	0.807
8	0.503	0.638	0.742	0.984
10	0.629	0.685	0.777	0.998
12	0.662	0.735	0.838	1.000

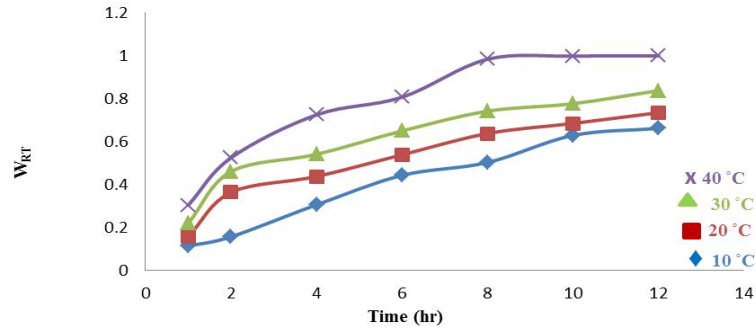


Figure 12. Relationship between water retention versus time.

Table.10. Results of fractional hydration (FH) at different time and temperature.

Time (hr)	Temperature °C			
	10 °C	20 °C	30 °C	40 °C
1	0.964	0.974	0.981	0.986
2	0.973	0.988	0.991	0.992
4	0.986	0.990	0.992	0.994
6	0.990	0.992	0.993	0.995
8	0.991	0.993	0.994	0.996
10	0.993	0.994	0.995	0.996
12	0.993	0.994	0.995	0.996

The results obtained are listed in Table 9 and 10, which are indicated that the water retention and fractional hydration are increase as well as the temperature increased until reach equilibrium with a values of 1 and 0.996 respectively as shown in Fig. 12 and 13.

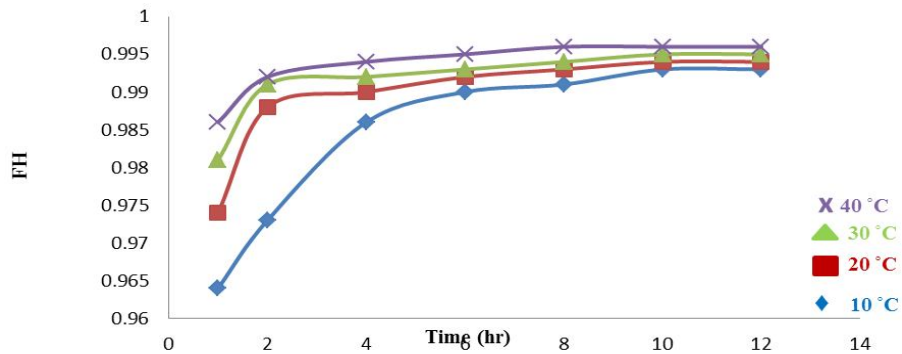


Figure 13. Relationship between FH versus time.

3.6. Swelling kinetic

In order to examine the controlling mechanism of the swelling processes, several kinetic models were used to test experimental data. The different chemical group on the polymeric chains imply that there are many types of polymer- solution interaction any kinetics are likely to be global. A simple kinetic analysis is a second- order equation in the form of:

$$\frac{dS}{dt} = k_{2,s} (S_{eq} - S)^2 \dots\dots\dots 8$$

Where $k_{2,s}$ is the rate constant of swelling and S_{eq} (or $S_{eq} \%$) denotes the swelling percent at equilibrium. After definite integration by applying initial conditions $S = 0$ at $t = 0$ and $S = S$ at $t = t$, Eq. 8 becomes

$$t / S = A + Bt \dots\dots\dots 9$$

where A is reciprocal of initial swelling rate r or $1/k_{2,s} S_{eq}^2$ and B is inverse of the degree of swelling at equilibrium[31]. To test the kinetic model, t/S versus t graph was plotted (Fig. 14). The calculated kinetic parameters are tabulated in Table 11. As can be seen from the results obtained that the kinetic model is in agreement with swelling experiment.

Table.11. Swelling kinetic parameters.

Model type	Parameters		
	* S_{eq}	k_2	R^2
Second order	303	1.1×10^{-4}	0.9945

* S_{eq} = The maximum (theoretical) swelling ratio (SR).

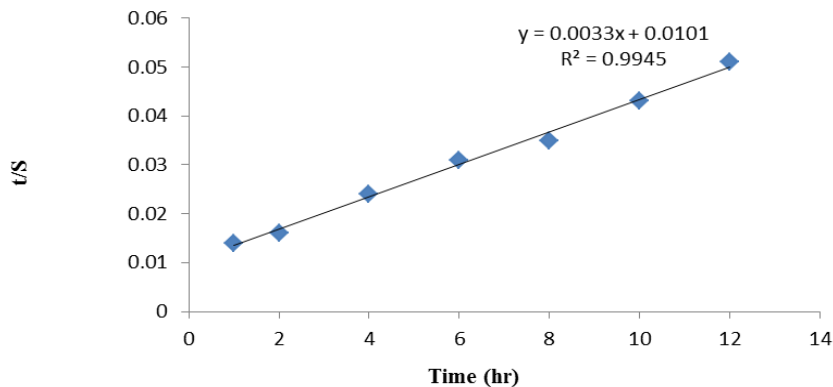


Figure 14. Second - order plots.

4. Conclusion

In present work, swelling properties of a commercially available (PAA) hydrogel bead were studied, and practical information on many different swelling parameters was predicated as a function of temperature and time. It was found that there is a clear relationship between swelling parameter and temperature which was increase as temperature increase. Kinetic mechanism was also studied and found to be fitted well with second order model. The maximum swelling percentage capacity was found to be 23370 at 12 hr.

5. References

- [1] Omidian, H., Rocca, J. G. and Park, K. **2005**, Advanced in superporous hydrogels, *J. Controlled Release*, pp. 102, 3-12.
- [2] Fernandez, E. Lopez, D., Lopez-Cabracos, E. and Mijangos, C. **2005**, Viscoelastic and swelling properties of glucose oxidase loaded polyacrylamide hydrogel and the evaluation of their properties as glucose sensors, *Polymer*, 46, pp. 2211- 2217.
- [3] Gupta, P., Vermani, K. and Garg, S., **2002**, Hydrogels from controlled release to pH-responsive drug delivery. *Drug Discovery Today*.7 (10), pp. 569-579.
- [4] Evmenenko, G., Alxev, V., Budtova, T., Buyanov, A. and Frenkel, S. **1999**, Swelling- induce changes of poly electrolyte gels. *Polymer*, 40, pp. 2975-2979.
- [5] Peppas, N., **1987**. *Hydrogels in medicine and pharmacy*, vol. 2. Boca Raton, FL, CRC Press.
- [6] AmEnde, M. and Peppas, N. **1996**, Transport of ionizable drug and proteins in crosslinked poly(acrylic acid) and poly(acrylic acid-co-2-hydroxyethyl methacrylate) hydrogels, *J. Appl. Polym. Sci.* 59(4), pp. 673-685.
- [7] Byrne, M., Park, K. and Peppas, N. **2002**. Molecular imprinting within hydrogels. *Adv. Drug Delivery Rev.* 54, pp. 149-161.
- [8] Grini, G. Recent developments in polysaccharide- based materials used as adsorbents I wastewater. *Prog. Polym. Sci.* 30, pp. 38-70.
- [9] Gombotz, R. and Hoffman, A. **1986**. Immobilization of Biomolecules and Cells on and within Synthetic Hydrogels. In. *Hydrogels in medicine and pharmacy*, vol.5. Peppas, N., Ed., Fundamentals CRC Press. Florida.
- [10] Peppas, N. and Mikos, A. **1986**. Preparation methods and structure of hydrogels, In. *Hydrogels in medicine and pharmacy*, vol.1. Peppas, N., Ed., Fundamentals CRC Press. Florida.
- [11] Güven, O., Şen, M., Karadağ, E. and Saraydin, D. **1996**. A review on the radiation synthesis of copolymeric hydrogels for adsorption and separation purposes, *Radiat. Phys. Chem.* 56, pp. 381-386.
- [12] Denizli, A., Say, R., Garipcan, B. and Patir, S. **2004**. Methacrylamide-doglutamic acid functionalized poly(2-hydroxy methacrylate) beads for $(\text{UO}_2)^{2+}$ removal. *Reactive & Functional Polymers* 58, pp. 123-130.
- [13] Zhung, A., Asakura, T. and Uchiyama, G. **2003**. The adsorption mechanism of uranium(VI) from seawater on a macroporous fiber polymeric adsorbent containing amidoxime chelating functional group. *Reactive & Functional Polymers* 57, pp. 67-76.
- [14] Dhodapkar, R., Borde, P. and Nandy, T. **2009**. Super absorbent polymer in environmental remediation, *Global NEST Journal* vol.11(2), pp.223-234.
- [15] Buchholz, F. and Graham, A. **1997**. Modern superabsorbent polymer technology, Wiley, New York.
- [16] Mahdavinia, G., Pourjavadi, A., Hosseinzadeh, H. and Zohuriaan, M. **2004**. Modified chitosan superabsorbent hydrogels from poly(acrylic acid-co-acrylamide) grafted chitosan with salt- and pH- responsiveness properties, *European Polymer Journal*, 40, pp. 1399-1407.
- [17] Cussler, E., Stokar, M. and Varberg, J. **1984**. Gels as size selective extraction solvents. *American Institute of Chemical Engineers*, 30, pp. 578-582.

- [18] Gehrke, S., Andrews, G. and Cussler, E. **1986**. Chemical aspects of gel extraction. *Chemical Engineering Science*, 41, pp. 2153-2160.
- [19] Freitas, R. and Cussler, E. **1987**. Temperature sensitive gels as extraction solvents, *Chemical Engineering Science*, 42, pp.97-103.
- [20] Badiger. M., Kulkarni, M. and Mashelkar, R. **1992**. Concentration of macromolecules from aqueous solution: a new swell process, *Chemical Engineering Science*, 47, pp.3-9.
- [21] Grodzinsky, A. and Grimshaw, P. **1990**. Electrically and chemically controlled hydrogel for drug delivery, *Pulsed and Self-Regulated Drug Delivery*. pp.47-64.
- [22] Vasheghani-Farahani, E. Cooper, D, Vera, J. and Weber, M. **1992**. Concentration of large biomolecules with hydrogels, *Chemical Engineering Science*, 47, pp. 31-40.
- [23] Davies, L., Novais, J. and Martins-Dias, S. **2004**. Influence of salts and phenolic compounds on olive mill wastewater detoxification using superabsorbent polymer, *Bioresource technology*, 95, pp. 259-268.
- [24] Mouayad Q. Al-Abachi, Nagam Shaker Al- Awady and Ahmed. M. Al-Anbakey, PhD. Thesis, *Study of The Efficiency of Some Metal Ions Entrapment in Crystalline Water Granules Using Different Spectrophotometric Methods*, University of Baghdad, Department of Chemistry, **2013**.
- [25] Musser, G.L. and Burger, W. F., (1997). In *Mathematics for Elementary Teachers, a Contemporary Approach*, Upper Saddle River, NJ: Prentice Hall, 4th ed. pp.507-641.
- [26] Erdener, K., Dursur, S. and Yasemin, C. **2006**. Swelling characterization of polyelectrolyte poly(Hydroxamic acid) hydrogels in aqueous thiazin dye solution, *Polymer-plastic Technology and Engineering* 45, pp. 729-734.
- [27] AmEnde, M. and Peppas, N. **1997**. Transport of ionizable drugs and proteins in crosslinked poly(acrylic acid) and poly(acrylic acid-co-2-hydroxyethyl methacrylate) hydrogels. II. Diffusion and release studies. *J. controlled Release* 48, pp. 47-56.
- [28] Uruzhezaki, F., Yamaguchi, H., Nakamura, K., Numajiri, S., Sugibayashi, K. and Morimoto, Y. **1990**. Swelling and mechanical properties of poly(vinyl alcohol) hydrogels. *Int. J. Pharm.* 58, 135-142.
- [29] Gupta, N. and Shevakumar, H. **2010**. Preparation and characterization of superporous hydrogels as gastro retentive drug delivery system for rosiglitazone maleate. *DARU* 18(3), pp. 200-210.
- [30] Kose, G., Kenar, H., Hasirci, V. and Hasirci, V. **2003**. Macro porous poly(3-hydroxybutyrate-co-3-hydroxyvalerate) matrices for bone tissue engineering. *Biomaterials*, 24, pp. 1949-1958.
- [31] Peniche, C., Cohen, M., Vazquez, B. and Roman, J. **1997**. Water sorption of flexible networks based on 2-hydroxyethyl methacrylate-triethylen-glycol dimethacrylate copolymers. *Polymer*, 38, pp. 5977-5982.