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EFFECT OF pH ON SWELLING PROPERTIES OF COMMERCIAL POLYACRYLIC ACID HYDROGEL BEAD

Ahmed. M. Saeed Al-Anbakey

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

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ABSTRACT:

The widespread application of hydrogels bead in a number of application like separation, adsorption, filtration, agriculture and drug delivery make it important to property understand the swelling properties of these materials. Typically, gel size and swelling capacity are sensitive to outer solution pH. In this paper, the study of the swelling capacity of the commercial polyacrylic acid hydrogel bead was investigated as a function of time and pH. The diameter, weight, degree of swelling, water retention as well as the fractional hydration were studied to predicate the swelling properties of hydrogel bead at a given pH. The type of diffusion and its related parameter diffusion exponent (n) and diffusion constant (k) were studied and calculated.

KEY WORDS: swelling properties**,** polyacrylic acid, hydrogel bead.

* Corresponding author

Dr. Ahmed. M. Saeed Al-Anbakey**,**
Email: dr.ahmedalanbakey@yahoo.com

INTRODUCTION:

Hydrogel are three-dimensional cross-linked polymeric net work, which swell significantly on contact with water or aqueous solution. Most hydrogels are formed by polymerization of monomers containing hydrophilic groups with multifunctional monomers or by groups of hydrophilic with polymers [1]. Hydrogels have found enormous application in bioengineering, biomedicine, photographic technology and many other [2]. The swelling properties of hydrogel are currently being exploited in a number of application including control of micro fluidic flow [3], muscle-like actuators [4,5], filtration/ separation [6] and drug delivery [7,8].

The structure and properties of hydrogel are similar to many biological tissues [9, 10]. Hydrogel net works 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 [11]. These polymers are used in many application including diapers and personal hygiene products, ion-exchange resins, membranes for hem-dialysis, ultra filtration and controlled release devices [12, 13].

The ability of PAA to swell extensively is facilitated by the carboxylic acid group on the polymer chain, which strongly associate with water molecules [14]. These groups are readily ionizable and sensitive to the changing of pH solution. Thus the swelling properties of the polyacrylic acid hydrogel bead are affected by the pH of the outer solution in which they are swelling [15, 16].

The focus of this paper is to enhance our current understanding on the effect of pH on the swelling properties of a commercial polyacrylic acid (PAA) hydrogel bead (i.e. size, weight, swelling ratio, swelling degree, water volume, and fractional hydration), the type of diffusion is also in our consideration in this study.

EXPERIMENTAL:

Materials

Distilled water, Hydrochloric acid (HCl) supplied from BDH and commercial polyacrylic acid (PAA) hydrogel bead were used.

Instrumentation

Ametrohm E.632 pH meter (Switzerland) with glass combination electrode was used throughout this study. Vernier caliper (Figure.1) 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.

Batch Experiment

The swelling properties of commercial PAA hydrogel bead in aqueous solution was performed using batch equilibrium technique. A series of plastic containers each one contain a 25 ml of distilled water with pH range of (1-6.3) were used. The hydrogel beads with 0.0382 g weight and 3.67 mm diameter were placed in each container, and left for contact time range of (1-8) h at room temperature. The water swelling ratio (WSR) of hydrogel bead was calculated by using the following equation: [17]

$$\boldsymbol{WSR = \frac{w_{H_2O}}{W_0}} \quad \text{……………} \ \mathbf{(1)}$$

Where $\boldsymbol{w_{H_2O}}$ is the weight of water (g) penetrates onto hydrogel bead and W_o is the initial weight of hydrogel bead (g) used. While the weight of water was calculated by using the following equation:

$$W_{H_2O} = (W_S - W_0) \ \text{……….} \ \mathbf{(2)}$$

Where W_s is the weight of swollen bead at time t (Fig. 2). All of the experimental results were the average of triplicate experiments, and the pH of solution was adjusted using 0.5 M HCl solution.

RESULTS AND DISCUSSION:

All of the results obtained are tabulated in Tables (1-10).

Effect of pH on bead diameter and weight

The results obtained are listed in Tables 1 and 2 revealed that diameter and weight of hydrogel bead are affected strongly at lower value of pH (1and 2) especially at the first and second hour of swelling process, that maybe due to the high concentration of H^+ which leaded to the protonate of all set of carboxylic group found in the internal structure of hydrogel bead [18], that causes the swell / deswell process, and finally decreasing in water penetration in the hydrogel bead, which cause decreasing in the diameter and weight of hydrogel bead.(Figures.3 and 4).

While at high value of pH (4-6.3) the hydrogel bead suffered a sharp increase in its diameter and weight that may be due to the decreasing in the osmotic pressure of H^+ [19], that cause the hydrogel to swell much more and finally a large increase in diameter and weight of hydrogel bead occurs. Other parameters which are related to diameter and hydrogel bead weight such as water weight (W_{H2O}), water volume (V_{H2O}), the W_{H2O} / W_o ratio and V_{H2O} / V_o were calculated and tabulated in Tables 3, 4, 5 and 6.

The results indicated that the values of parameter are too small at the lower pH values and then these values increase with time and pH values increasing until reached 156.85 and 139.61 for W_{H2O} / W_o and V_{H2O} / V_o respectively at 8 hr and pH value of 6.3 as shown in Figures.5, 6, 7 and 8.

Determination of swelling ratio

The swelling ratio of hydrogel bead was calculated according to the following equation:

$$SR = \frac{W_i}{W_o} \quad \text{..........} \qquad (3)$$

Where W_i is the weight of swollen hydrogel bead at equilibrium or at time t. While swelling degree (swelling percentage) was calculated as following:

SD = SR X 100 ……….. (4)

The obtained results are listed in Table 7, revealed that the value of SR was small at the higher concentration of H^+ (pH value of 1 and 2), that causes the protonate the all carboxylic groups which are found in the internal structure of hydrogel bead, which was leaded to more interaction between the hydroxyl and carboxylic group due to forming of more hydrogen bound, that cause the decrease in internal volume of hydrogel bead and finally the decrease in the penetrate water as shown in Figure.9.

While at pH of range 4-6.3 the results shows a sharp increase in the value of swelling degree as shown in Figure.10.

Determination of water retention

The following equation was used to determine the water retention (W_{RT}) as a function of time at different pH values.[20]

$$W_{RT} = \frac{(W_t - W_d)}{(W_s - W_d)} \quad \text{...........} \; (5)$$

Where W_d is 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 time t. The results obtained are tabulated in table 8, which is shown that the W_{RT} almost constant value at lower pH values, while a sharp increasing is take place at higher value of pH as shown in Figure.11.

Determination of fractional hydration

The following equation was used to determine the water fractional hydration (WFH) as a function of time at different pH values.[2I]

$$WFH = \frac{(W_t - W_o)}{W_t} \quad \text{..........} \; (6)$$

Where W_t is the weight of swelled hydrogel bead at time t, W_o is the weight of the dried hydrogel bead. The results obtained are summarized in Table 9, and Figure.12, shows a plot of WFH vs. time at different pH.

Diffusion study

The following equation is used to determine the nature of diffusion of water into hydrogel bead:[22]

$$F = kt^n \quad \text{............} \; (7)$$

Where F is the fractional hydrate uptake at time t, 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 (Figure.13).

The results obtained are tabulated in Table 10, which is revealed that the diffusion behavior is anomalous transport behavior (non-Fickian) due to the value of n which is more than 0.5. That means the relaxation and diffusion time are the same order of magnitude [23].

CONCLUSION:

This study has given the quantitative information on the water swelling of the commercial PAA hydrogel bead. The effect of pH on the swelling was investigated through the calculated of some swelling parameters. It was found that there is a strong relation between pH values and the calculated swelling parameter. Diffusion of water onto PAA hydrogel bead has been found as non-Fickian in character.

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Figures:

Figure 1. Vernier calliper used for measuring the diameter of gel bead.

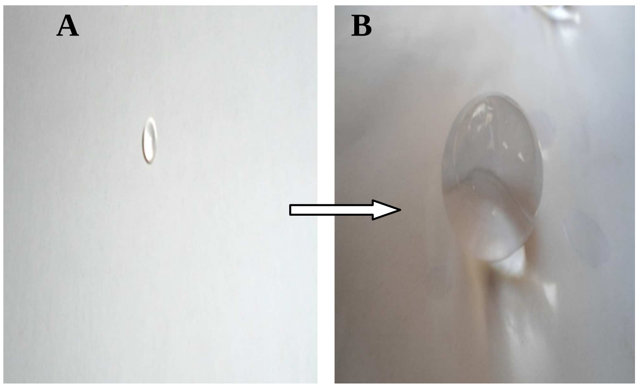

Figure 2. Profile and size of gel bead before (A) and after (B) swelling.

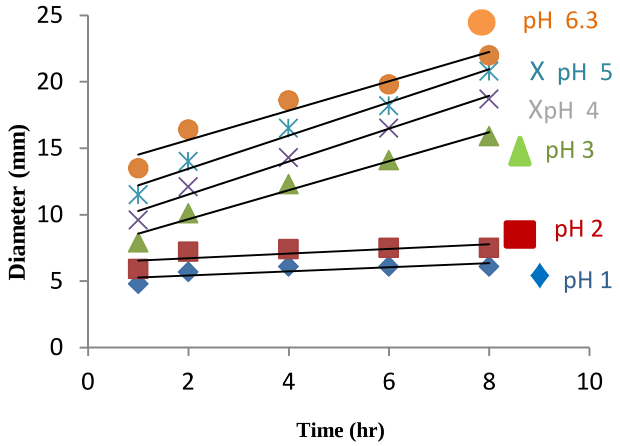

Figure 3 . The relationahipe between time and diameter of hydrogel bead at different pH

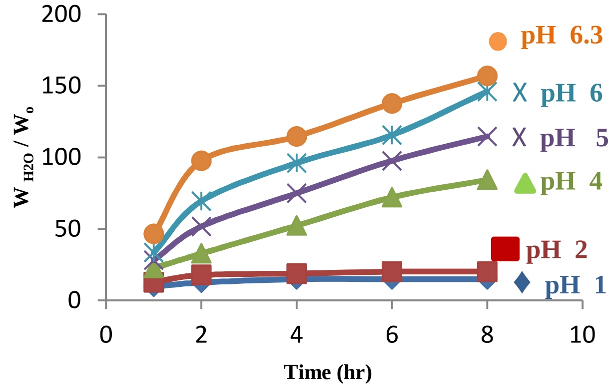

Figure 6 . The relationshipe between time and W_{H2O} / W_o at different pH

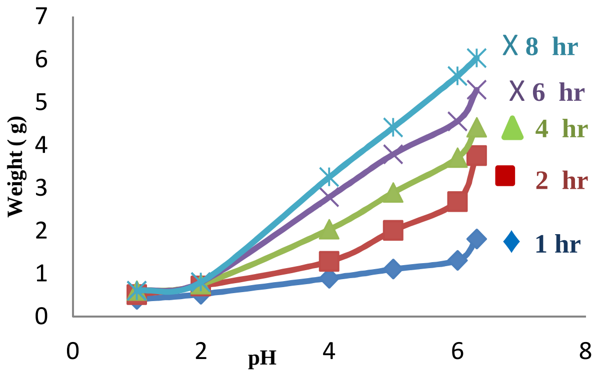

Figure 4 . The relationshipe between weight of hydrogel bead after swelling and pH

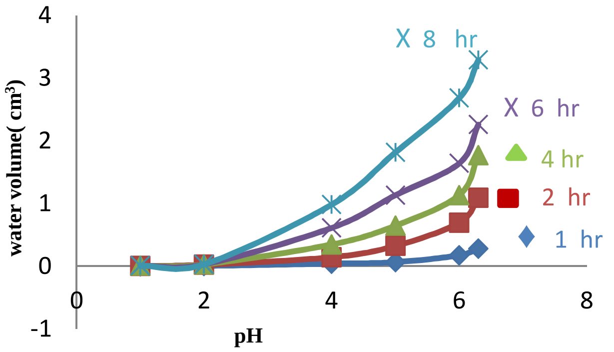

Figure 7 . The relationshipe between water volume and pH at different time

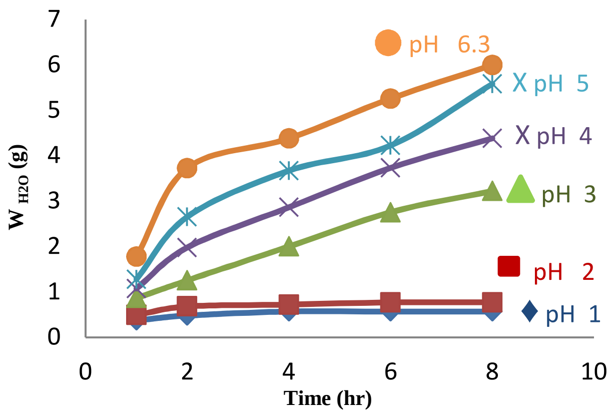

Figure 5 . The relationshipe between time and water weight at different pH

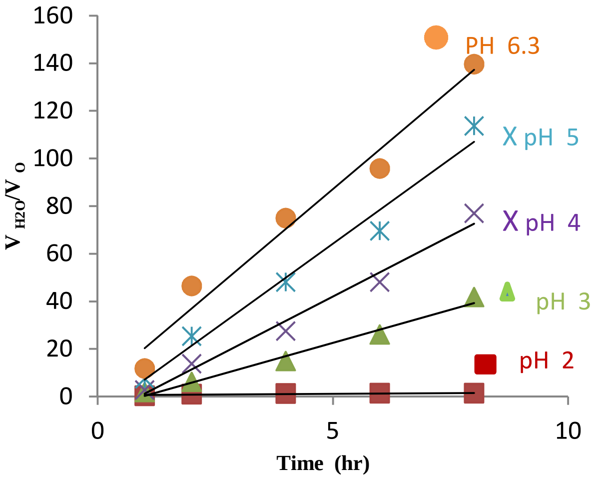

Figure 8 .The relationshipe between V_{H2O}/V_o and time at different pH

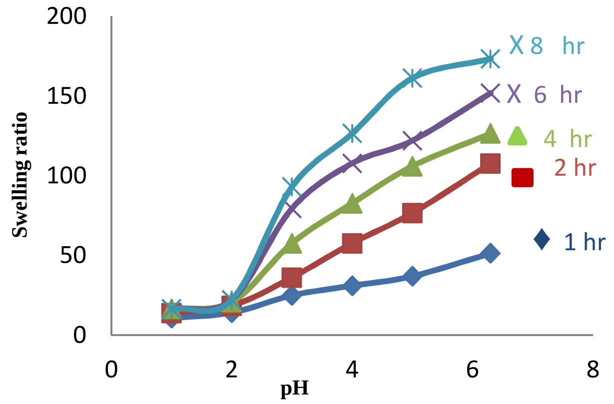

Figure 9 .The relationshipe between swelling ratio and pH at different time

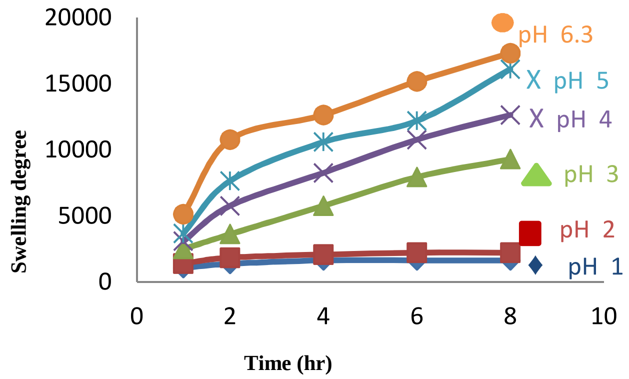

Figure 10 .The relationshipe between swelling degree and time at different pH

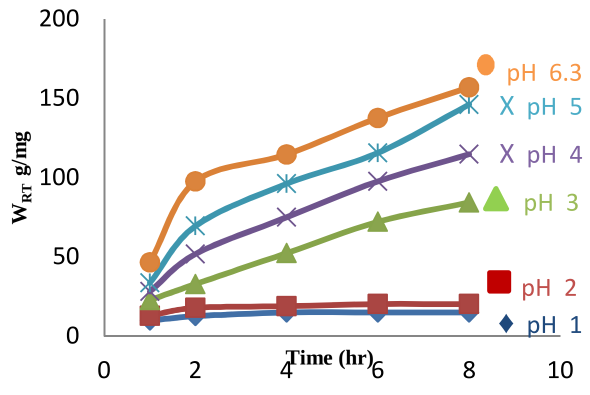

Figure 11 . The relationshipe between W_{RT} and time at different pH

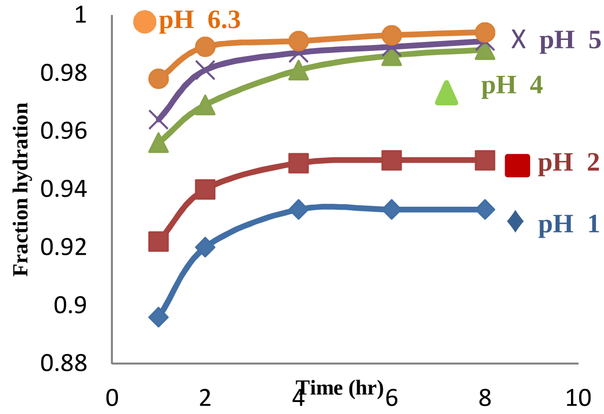

Figure 12 . The relationshipe between time and water fraction hydration at different pH

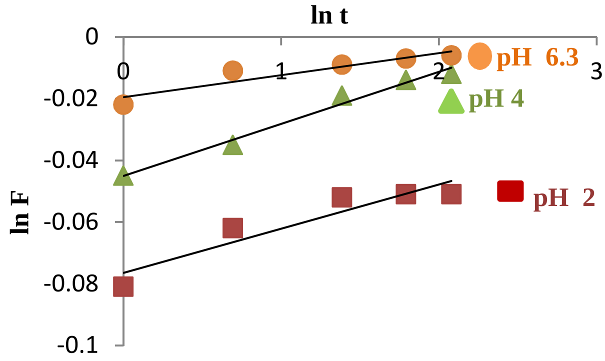

Figure 13. Plot of ln F vs. ln t for commercial PAA hydrogel bead at different pH.

Tables:

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

Time (hr)	pH					
	1	2	4	5	6	6.3
1	4.8	5.9	7.9	9.6	11.5	13.5
2	5.7	7.2	10.1	12.1	14.0	16.4
4	6.1	7.4	12.3	14.3	16.5	18.6
6	6.1	7.5	14.1	16.5	18.2	19.8
8	6.1	7.5	15.9	18.7	20.8	22.0

Table 2. Results of the weight (g) of hydrogel bead after swelling at different time and pH.

Time (hr)	pH					
	1	2	4	5	6	6.3
1	0.4066	0.5266	0.9006	1.1106	1.3156	1.8136
2	0.5156	0.7166	1.2896	2.0136	2.6886	3.7636
4	0.6046	0.7566	2.0357	2.8986	3.7066	4.4136
6	0.6046	0.8066	2.7896	3.7896	4.5596	5.2936
8	0.6046	0.8066	3.2576	4.4166	5.6156	6.0340

Table 3. Results of the weight of water (g) entrapped onto hydrogel bead at different time and pH

Time (hr)	pH					
	1	2	4	5	6	6.3
1	0.3684	0.4884	0.8624	1.0724	1.2774	1.7754
2	0.4774	0.6784	1.2514	1.9754	2.6504	3.7254
4	0.5664	0.7184	1.9975	2.8604	3.6684	4.3754
6	0.5664	0.7684	2.7514	3.7514	4.2214	5.2554
8	0.5664	0.7864	3.2194	4.3784	5.5774	5.9958

Table 4. Results of W_{H2O} / W_o at different time and pH.

Time (hr)	pH					
	1	2	4	5	6	6.3
1	9.64	12.79	22.58	28.07	33.44	46.48
2	12.50	17.76	32.76	51.71	69.38	97.52
4	14.83	18.81	52.29	74.88	96.03	114.54
6	14.83	20.12	72.03	97.60	110.51	137.58
8	14.83	20.12	84.28	114.62	146.01	156.85

Table 5. Results of the volume of water (cm^3) penetrate onto hydrogel bead at different time and pH.

Time (hr)	pH					
	1	2	4	5	6	6.3
1	0.001	0.007	0.043	0.067	0.175	0.280
2	0.005	0.025	0.145	0.326	0.696	1.091
4	0.009	0.030	0.349	0.649	1.135	1.772
6	0.009	0.032	0.613	1.135	1.643	2.261
8	0.009	0.032	0.984	1.818	2.684	3.290

Table 6. Results of V_{H2O} / V_o at different time and pH.

Time (hr)	pH					
	1	2	4	5	6	6.3
1	0.04	0.28	1.82	2.84	7.42	11.86
2	0.22	1.07	6.14	13.81	25.25	46.54
4	0.38	1.26	14.79	27.50	48.09	74.90
6	0.38	1.36	25.97	48.09	69.64	95.76
8	0.38	1.36	41.69	77.03	113.72	139.61

Table 7. Results of swelling ratio at different time and pH.

Time (hr)	pH					
	1	2	4	5	6	6.3
1	10.7	14.1	24.9	31.0	36.9	51.3
2	13.8	18.5	36.2	57.7	76.6	107.7
4	16.4	20.8	57.7	82.7	106.0	126.5
6	16.4	22.2	79.5	107.8	122.0	151.9
8	16.4	22.2	93.0	126.5	161.2	173.3

Table 8. Results of water retention onto hydrogel bead at different time and pH.

Time (hr)	pH					
	1	**2**	**4**	**5**	**6**	**6.3**
1	0.061	0.082	0.144	0.180	0.213	0.296
2	0.080	0.113	0.210	0.331	0.442	0.622
4	0.095	0.120	0.335	0.480	0.612	0.780
6	0.095	0.128	0.461	0.625	0.750	0.883
8	0.095	0.128	0.540	0.735	0.900	1

Table 9. Results of water fractional hydration of hydrogel bead at different time and pH.

Time (hr)	pH					
	1	**2**	**4**	**5**	**6**	**6.3**
1	0.896	0.922	0.956	0.964	0.970	0.978
2	0.920	0.940	0.969	0.981	0.986	0.989
4	0.933	0.949	0.981	0.987	0.989	0.991
6	0.933	0.950	0.986	0.989	0.991	0.993
8	0.933	0.950	0.988	0.991	0.993	0.994

Table 10. Results of n and k of hydrogel bead at different pH.

pH	**n**	**k x 10^{-2}**
1	0.902	1.95
2	0.926	1.44
4	0.983	1.69
5	0.967	1.27
6	0.974	1.01
6.3	0.981	0.7

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