EG0100013

Seventh Conference of Nuclear Sciences & Applications
6-10 February 2000, Cairo, Egypt

Rad.C-1 Removal of Some Basic Dyes by Poly (Vinyl Alcohol / Acrylic Acid) Hydrogel

El-Sayed A. Hegazy, Samya E. AbdEl-Aal, H.A. AbdEl-Rehim, Nevien A. Khalifa* and Erwaa M. El-Hosseiny.

National Center for Radiation Research and Technology, P.O.Box 29, Nasr City, Cairo, Egypt.
**Faculty of Science, Helwan University, Helwan, Egypt.*

ABSTRACT

A Study has been made on the preparation and properties of poly (vinyl alcohol / acrylic acid) hydrogel for the purpose of removal of cationic dyes from aqueous solutions. The effect of dose and monomer concentration on the uptake property of the hydrogel toward dye was studied. The uptake of basic methylene blue-9 dye with PVA/AAc was studied by the batch adsorption technique. The effect of pH on the dye uptake was demonstrated to find out that the suitable pH for maximum uptake occurred at pH 5. It was observed that as the concentration of dye is increased the dye uptake decreased. Furthermore, the uptake of dye by hydrogels increased as the temperature was elevated. The recovery of dye adsorbed is possible by treating the hydrogel with 5% HCl. The results obtained suggested that this hydrogel possessed good removal properties towards basic methylene blue-9 dye, and this suggests that such hydrogels could be acceptable for practical uses.
Keywords: *(Radiation polymerization, poly (vinyl alcohol), acrylic acid, dyes removal, properties)*

INTRODUCTION

Development is demanded in the technology of wastewater treatment after the industrial expansion caused problems of pollution and water resources in this country. Many techniques such as reverse osmolysis, ozonozation or the application of radiation processing to the waste water treatment were studied.[1,2,3] Most dyes used by textile industry are not easily degraded by ordinary treatment processes.[4]

The removal of color from textile wastewater is a major environmental problem because of the difficulty of treating such waters by conventional methods. Colored waters are also objectionable on aesthetic grounds for drinking and other municipal and agricultural purposes. Some groups have used various adsorbents for the removal of acidic and basic dyes from aqueous solutions.[5] Hydrogels are crosslinked hydrophilic polymers that swell in water, usually to equilibrium. Hydrogels have wide spread applications in bioengineering, biomedicine, pharmaceuticals, veterinary, food industry agriculture, photographic technology, and others. They are also used as controlled release systems of drugs, for the production of contact lenses and artificial organs in biomedicine, as an adsorbent for the removal of some agent in environmental applications.[6]

Poly (vinyl alcohol) PVA is a well-known material as a highly hydrophilic polymer, and of ease availability. Investigations have been done on its use in the field of separation processes.[7,8] However, such a polymer suffers from poor water resistance and low mechanical strength in aqueous solutions. Therefor, it has to be turned into a complete insoluble stable material with good mechanical properties. A number of investigations have been reported in the literature to modify PVA by crosslinking with different reagents such as aldehyde[9], dicarboxylic acid[10], heat[11], H_3BO_3[12], and radiation[13,14]

Radiation methods have been particularly studied for the production of a large variety of graft copolymers having interesting properties.[15] Extensive work has been performed on methods for

optimizing yields when monomers are radiation-copolymerized with the backbone polymer, especially with a simultaneous technique.[16, 17]

The purpose of this investigation was to study and control the insolubility of PVA, thereby creating a permanent polymeric hydrogel. Modification by copolymerization with acrylic acid Poly (vinyl alcohol)/acrylic acid (PVA/AAc) using gamma rays as an initiator, and the factors that affect such copolymerization process are the topics of this study. In addition, a trail was made for the recovery of cationic dyes from wastewater using the prepared Hydrogel.

EXPERIMENTAL

Materials

Poly (vinyl alcohol) (PVA) obtained from Laboratory Rasayan. S.d. Fine-Chem. Ltd. of M.W. app. 1,25,000. Acrylic acid (AAc) (Merck, Germany) of purity 99%, was used without further purification. The other chemicals, such as crosslinker, dye and buffers were reagent grade and used as received.

Preparation of Hydrogel

A (5 gm) of PVA is dissolved in (100 ml) distilled water and is mixed with N,N-Methylenediacrylamide (0.5 gm) as a cross-linker. Different amounts of AAc are added to 20 ml of the mixture previously prepared, depending on the required PVA/AAc composition. This mixture is then exposed to Co-60 gamma irradiation at dose rate (8.6) kGy/h .The hydrogel is left to dry at room temperature.

Dye Uptake Measurements

The prepared hydrogels (about 0.5 g) thus obtained are soaked in 50 ml solution of cationic dye. Effect of time on the uptake process is measured and then the solution is allowed to equilibrate for 24 h. The UV absorbency of dye solution was measured at a wavelength 666 nm. The concentrations of the dye solutions were determined from the standard calibration curve previously determined.

X-Ray Diffraction (XRD):

X-ray diffraction patterns were obtained with a XD-DI Series, Shimadzu apparatus using nickel-filtered and Cu-Kα target. This technique was performed to clarify the changes in morphological structure caused by the copolymerization.

Thermal Analysis:

Thermal analysis was made using Thermal Gravimetric Analysis (TGA), Shimadzu TGA system of Type TGA-50 in nitrogen atmosphere 20 ml/min. The temperature range was from ambient to 500°C at heating rate of 10°C/min.

FTIR Spectroscopy:

Analysis by infrared spectroscopy was carried out using Mattson 1000,Unicam, England in the range from 400-4000 cm^{-1}.

Ultraviolet Spectroscopy (UV):

Analysis by a UV spectrophotometer was carried out using a Milton Roy spectronic 1201 in the range from 190 to 900° nm.

pH Measurement:

The pH of the dye solutions was determined using Jenway 3310 pH Meter.

RESULTS AND DISCUSSION

This study aims to prepare copolymer hydrogel having functional groups by radiation induced copolymerization process which is suitable for the removal of some basic dyes from wastewater.

Preparation of Hydrogel

Ionic hydrophilic hydrogel was prepared by radiation-induced copolymerization of PVA/AAc aqueous solution in the presence of N,N-Methylenediacrylamide as a cross-linker using gamma-irradiation. The influence of PVA/AAc composition at different dose on the gel percent, i.e. the insoluble hydrogel is studied and shown in Figure (1). It is observed that as the AAc content increases the gel percent increase, Then it tends to level off at a composition of 50/50-wt.% of PVA/AAc. This behavior is observed for all irradiation doses used here. Meanwhile, the higher the dose, the higher the gel percent obtained, at a given composition.

Results showed that the cross-linking process in the prepared hydrogel is enhanced at higher dose as well as for AAc-rich solution.

This is a typical behavior for this system that having water soluble monomer AAc and polymer. The use of 50/50-wt.% composition at 30 kGy resulted in 100% gelled hydrogel. However, from the practical point of view, the hydrogel should possess some suitable porosity and hydrophilicity for the purpose of adsorption processes. Therefor, 60/40-wt.% composition is selected to be the best condition for the preparation of required hydrogel that can meet the requirements of dye adsorption from their wastes.

Swelling Behavior

The swelling parameter is a very important factor for the applicability of such hydrogel. Figure (2) shows the effect of dose on the water uptake at different temperatures. It is clear that as the irradiation dose increases the water uptake decreases, at a given temperature. Meanwhile, no very significant effect on the temperature is observed. This is reasonably understood by considering the crosslinking process that is enhanced at higher doses, which restricts and hinders the diffusion of water through the network structure. In addition, due to the relatively high swelling value, the temperature has no more effect on such process of water adsorption.

Effect of Treatment Time

Treatment time is of great importance from the economical point of view. Figure (3) shows the effect of treatment time on the dye uptake at different temperature. Initially, the dye uptake increases sharply with time to reach the Equilibrium State within 60 min, at elevated temperature, but it takes about 120 min at ambient temperature. At the mean time, the uptake of the dye is improved at higher temperature. This can be reasonably understood by the enhanced diffusion at such elevated temperature.

Effect of Copolymer Composition on Dye Uptake

Figure (4) shows the effect of PVA/AAc composition on the dye uptake percent. It is very interesting to find that the incorporation of PAAc in the copolymer even with 20 %, resulted in a sharp increase in dye uptake percent (about 95 %). Such uptake percentage is kept constant for the compositions up to 50/50-wt. %. Thereafter, it decreases as the AAc content increases up to 80 %. However, it again increases for the pure PAAc to absorb almost 92 % of dye, which is similar to that of 50/50-wt. % composition. This indicates that the dye uptake is mainly dependent on the amount of carboxylic functional groups in the hydrogel. However, PVA has a great role in this process as a hydrophilic porous hydrogel that having high affinity towards swelling in water. This behavior facilitates the diffusion of dye through its matrices.

Effect of pH

Figure (5) shows the effect of pH of feed solution on the dye uptake % for different hydrogel compositions. It is obvious that the dye uptake is enhanced in the acidic medium and is lowered in higher pH media. This behavior is observed for all hydrogel compositions in which the higher the acrylic acid content the higher the dye uptake. It seems that such basic dye is highly adsorbed in the acidic medium which is a normal behavior.

Effect of Dye Feed Concentration

Figure (6) shows the effect of dye feed concentration on the adsorption capacity of hydrogel at different pH's. It can be seen that the adsorption capacity increases as the feed concentration increases to reach a certain limiting value, which is higher at low pH if compared with those, obtained at high pH media. The adsorption capacity reaches to level off at 80 ppm feed concentration for pH 3 and 7, however, it reaches early at pH 10. This result is good agreement with that obtained in aforementioned results.

Thermal Stability

From the practical point of view, the prepared hydrogel should possess good thermal stability in the range of applicable temperature. Figure (7) and Table (1) shows the thermal diagrams for different hydrogel compositions at various elevated temperatures. It can be seen that in the initial stage of thermal diagram in the range from ambient temperature to 200°C, the weight loss is due to dehydration process of the water contained in such hydrophilic hydrogel. At the second stage from 200 to 350°C, there is decomposition in the side groups and branches in the hydrogel. However, at the third stage above 350°C, the weight loss is due to the main chain scission in the polymer chain and matrices. Results showed that such hydrogel is thermally stable at temperature up to about 300°C, which is suitable for practical use.

Change in Crystallinity

Figure (8) shows the XRD patterns for the prepared hydrogels that have different PVA/AAc compositions. No very significant change in PVA crystallinity is observed via the incorporation of PAAc chains in the copolymer. This is coincident with the FTIR Spectra for PVA and PVA/AAc copolymer (Fig. 9). The characteristic absorption bands for PVA are appeared and they are broadening for PVA/AAc copolymer. The FTIR Spectrum for PVA indicates also that it still has poly (vinyl acetate) in its structure due to the appearance of C=O groups at 1750 cm^{-1}.

CONCLUSION

It can be concluded that the prepared hydrogel by means of radiation-induced copolymerization of PVA/AAc solution is of interest in some practical uses such as in wastewater treatment from industrial waste dyes. It possesses good thermal stability and hydrophilic properties, which may make it acceptable for practical uses. Such hydrogel has high affinity towards adsorption of basic dyes and this is an advantage property over the traditional degradation methods for treating such waste in which more compounds that are toxic may result.

REFERENCE

1. M.Washino, Radiat. Phys. Chem. Vol. 18, No. 1-2, pp. 383-388, 1981
2. N.A.Vysootskaya (et al), Radiat. Phys. Chem. Vol. 28, No. 5/6, pp. 469-472, 1986
3. R.D. Morris and T.F. Craft, International Journal of Applied Radiation & isotopes, Vol. 24, pp. 245-52,1973
4. Nobutake Suzuki (et al), International Journal of Applied Radiation & Isotopes, Vol. 26, pp. 726-730 1975
5. Erdener Karadag (et al) Water, Air, and Soil Pollution 106: 369-378, 1998
6. Nurettin Sahiner (et al) Polymer Bulletin 41, 371-378 (1998)
7. F.T Burczak,.; Y. Ikada, Proc Jpn Acad Ser B 1991, 75(5), 83.
8. V.Shantora; R. Y. M. Huang, J Appl Polym Sci 1981, 26, 3223
9. Koyama,K. (et al) J Appl Polym Sci 1982, 27, 2845
10. S. Peter; R. Stefan; In the Proceedings of the International Symposium of Fresh Water from the Sea; E. Delyannis, Ed.; Athens, 1980; Vol. 2, p 197
11. M. G. Katz; T. Wydeven; J Appl Polym Sci 1982, 27, 79.
12. S. Peter; N. Hense; R. Stefan; Desalination 1976, 16, 161.
13. M. G. Katz; T. Wydeven; J Appl Polym Sci 1981, 26, 2935
14. H. A. Abd El-Rehim, El-Sayed Hegazy, A. M. Ali J Appl Polym Sci, Vol. 74, 806-815, 1999
15. H. A . Abd El-Rehim; A. M. Ali; H. G.Nowier; E. A. Hegazy; H. F. Aly, In Proceedings of the Sixth Conference on Nuclear Sciences and Applications, Cairo, Egypt, March 15-20, 1996; Vol. 3, p 227
16. E. A. Hegazy; N. H.Taher; A. R.Ebaid; J Appl Polym Sci 1990, 41, 2637
17. E. A. Hegazy; H. A. Abd El-Rehim; N.A. Khalifa; A. El-Hag Ali, J Radiat Phys Chem, in press

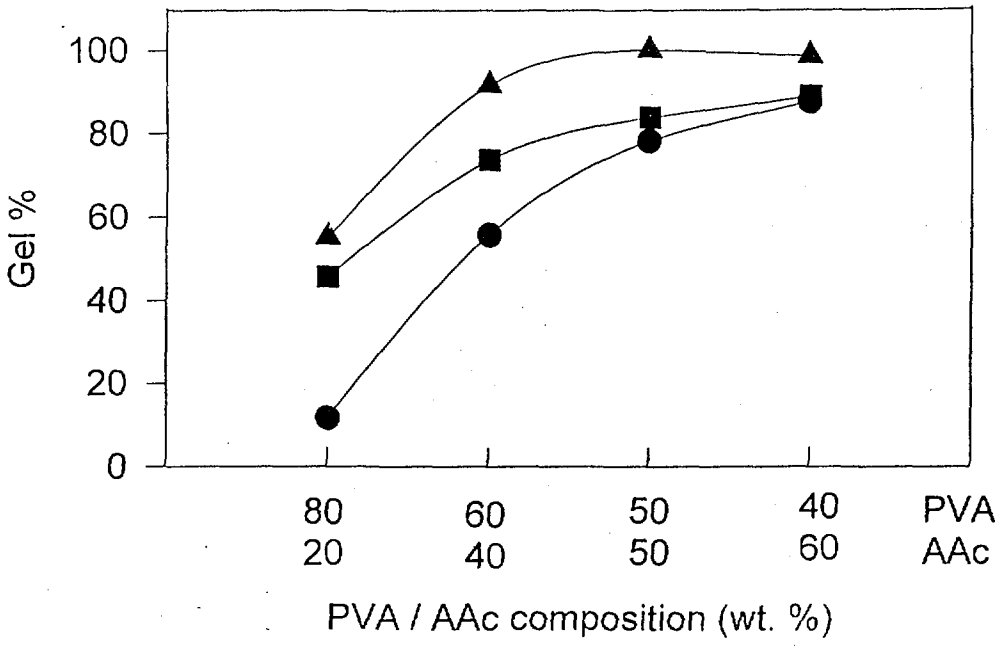


Fig.(1): Effect of (PVA/AAc) composition on Gel % at different doses (kGy); (●)10, (■)20, and (▲)30. N-N methylene di-acrylamide concentration (10 wt.%) as a cross-linker

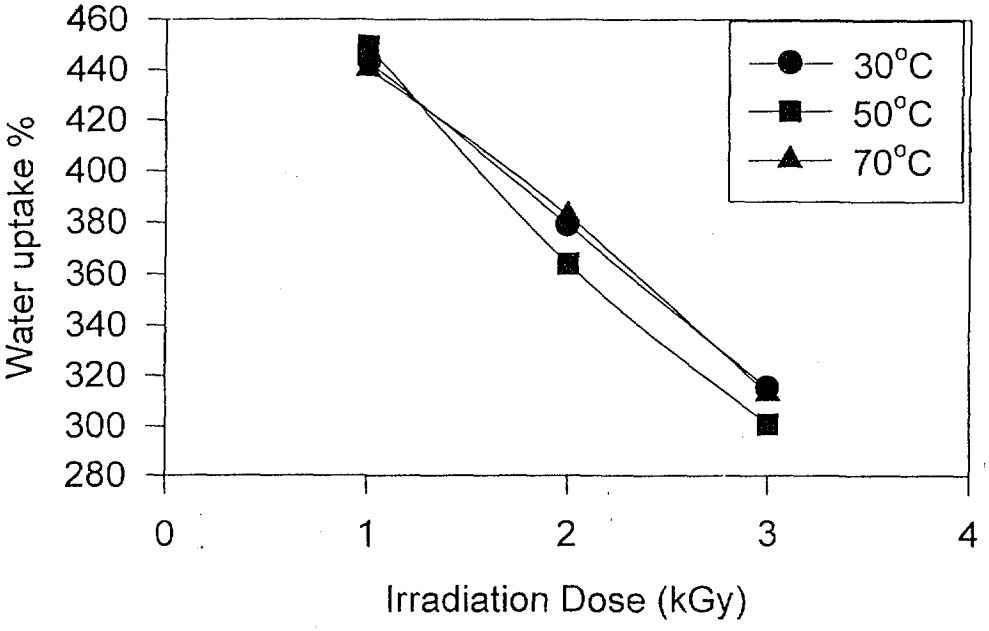


Fig.(2): Effect of irradiation on water uptake % at different temperatures. PVA/AAc composition; 60/40-wt.%. Swelling time 24hr.

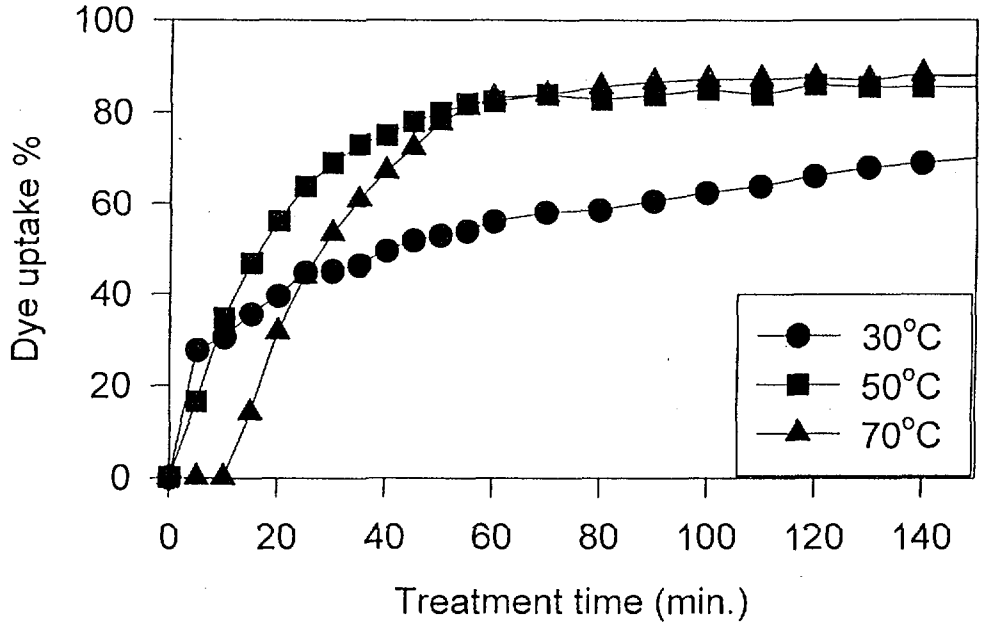


Fig.(3): Effect of treatment time on the dye uptake% at different temperature. For the PVA/AAc composition 60/40 wt%.

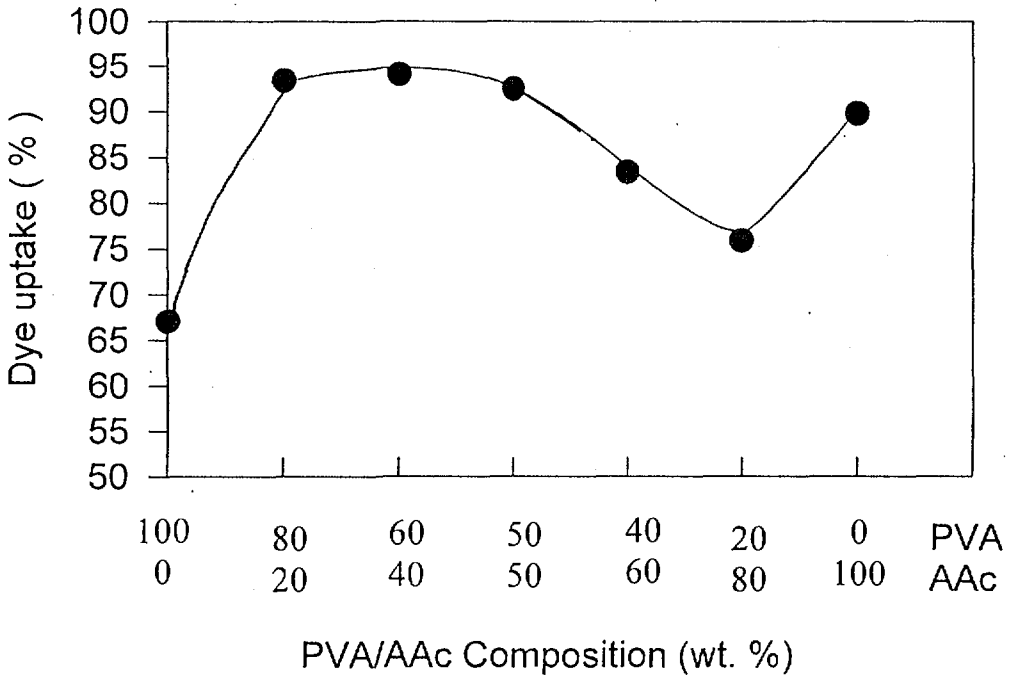


Fig.(4): Effect of different (PVA/AAc) compositions on dye uptake %. At room temperature(30°C), irradiation dose 20 kGy. Treatment time 3 hours

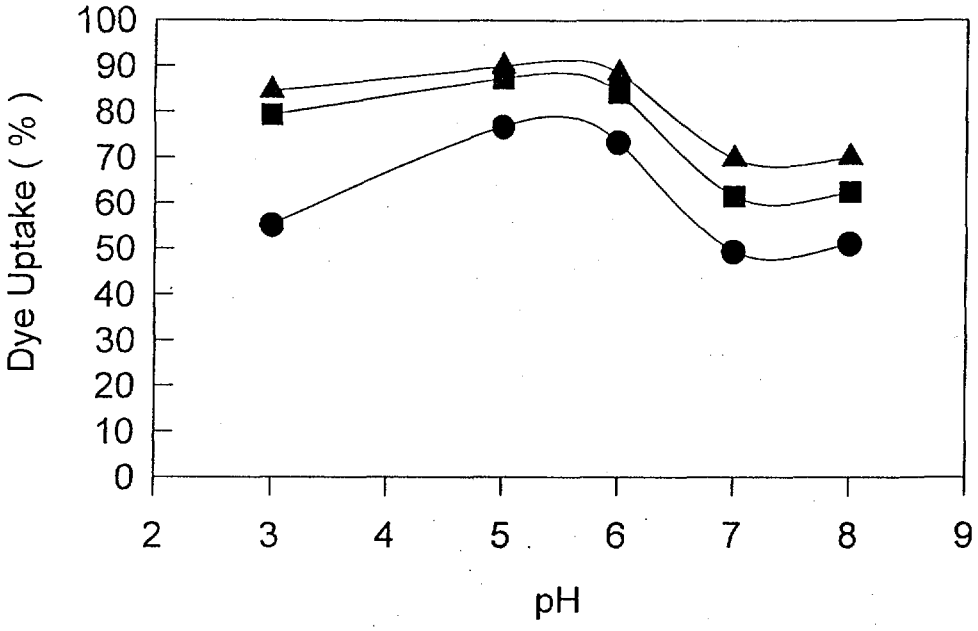


Fig.(5): Effect of pH on the uptake% of basic Methylene Blue (10 ppm) for different PVA/AAc compositions : ( )80/20, ( )60/40, ( )50/50. At equilibrium time.

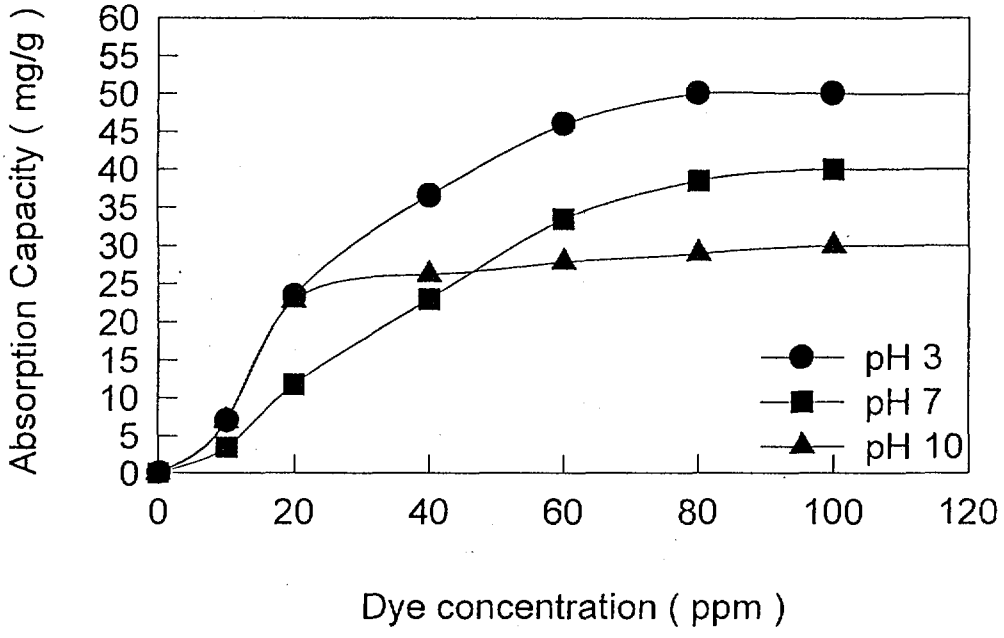
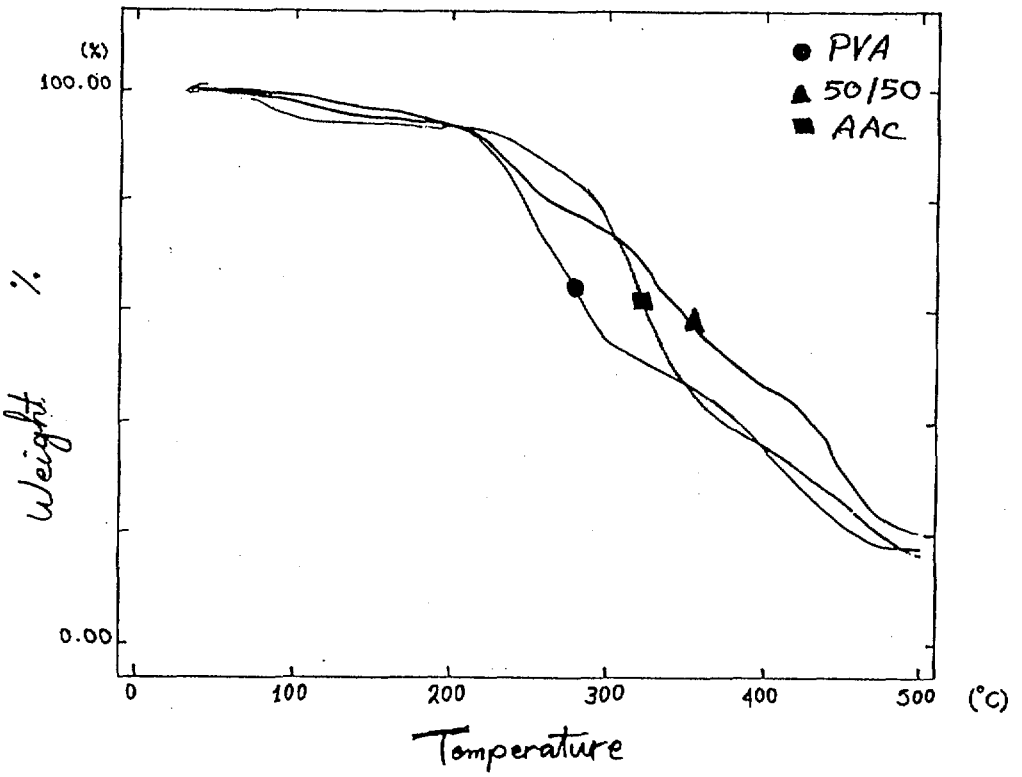
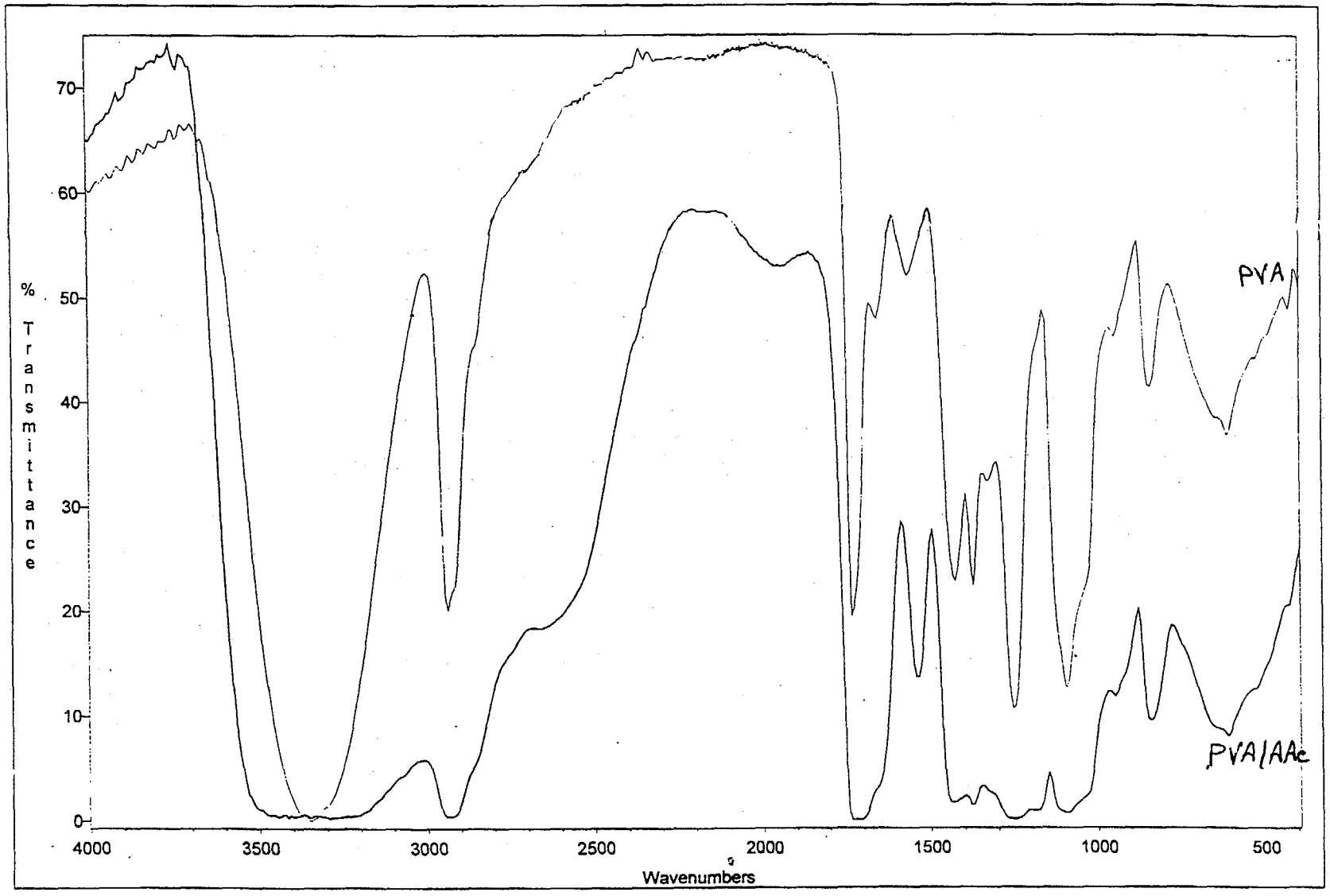


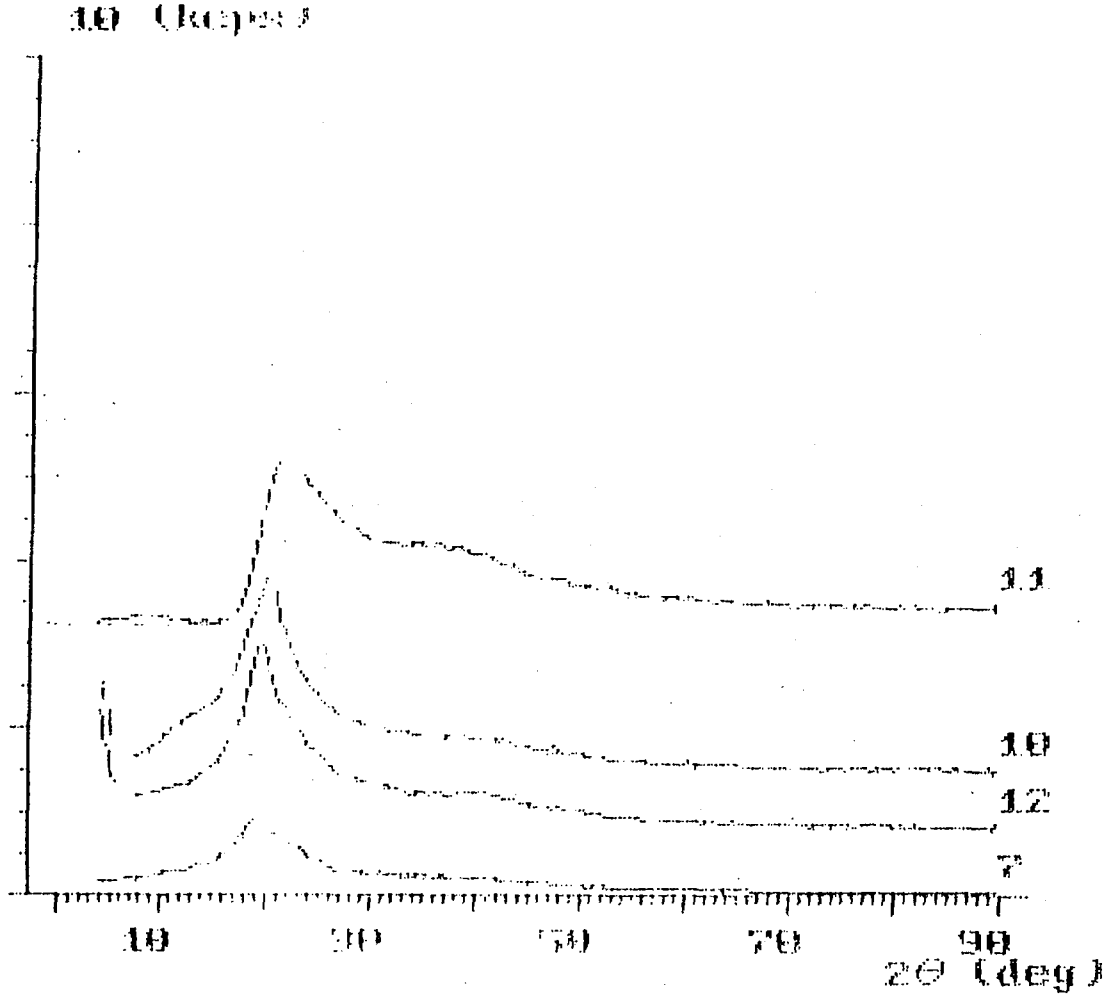
Fig.(6): Effect of feed solution concentration on the adsorption capacity for the prepared hydrogel at different pH

Table (2): Effect of PVA/AAc composition on the thermal stability of the copolymer at various elevated temperatures.

PVA/AAc composition	Weight loss (%)			
	200°C	300°C	400°C	500°C
Pure PVA	6.4	23.6	64	83.2
80/20	3.9	23.2	51.2	78.5
60/40	5.2	23.2	53.2	82
50/50	4.4	24.8	54	80.8
40/60	5.2	24	55.2	84.8
20/80	4.4	27.2	57.6	78.8
Pure AAc	5.6	44.4	64.8	81.6




70
60
50
40
30
20
10
0
% Transmittance
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers
PVA
PVA/AAc


1.1
1.0
1.2
2θ (deg.)