

# $\gamma$ -Irradiated Polyvinyl Alcohol (PVA) and Citric Acid Blend Hydrogels: Swelling and Absorption Properties

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## Abstract

$\gamma$ -Irradiated polyvinyl alcohol (PVA)/Citric acid blend hydrogels were prepared. Effect of radiation dose on gel fraction and swelling properties were observed. Effect of pH and NaCl concentration on swelling ratio, water absorption and water desorption of  $\gamma$ -irradiated hydrogels were studied. It was found that gel fraction attains maximum up to a certain dose but swelling ratio as well as water absorption decreases with increase in radiation doses. Swelling properties decreases with the increase in concentration of NaCl solution too and increases with the increase of pH.

**Keywords:**  $\gamma$ -Irradiation; Poly (Vinyl alcohol); Citric acid; Hydrogel; Swelling ratio; Water absorption; Water desorption

## Introduction

Hydrogels are defined as two or multi component systems consisting of a three dimensional network of polymer chains and water that fills the space between macromolecules. They have some important properties e.g., the ability to absorb aqueous solutions without losing shape and mechanical strength, are commonly met in many natural constituents of a human body, like muscles, tendons, cartilages, etc. Besides that, Hydrogel usually exhibit good biocompatibility in the contact with blood, body fluids and tissues. So it is widely used in the field of biomedicine [1] and pharmacy [2]. Hydrogel from synthetic polymers such as PVA, poly vinyl pyrrolidone (PVP), polyethylene oxide etc. have been studied but their properties need to improve further for special applications like wound dressing [3]. The mechanical properties of poly (vinyl alcohol) (PVA) hydrogel was improved by incorporation of chemical and physical crosslinking by formaldehyde [4] and crystallization [5]. Hydrogels of natural polymers, especially polysaccharide also have been used recently because of their unique properties such as non-toxic, biocompatible, biodegradable and abundant [6] to improve some properties like gel strength, swelling ratio, etc. Sago starch, a polysaccharides improve the gel strength and reduce the swelling ratio [7] of PVA hydrogel, but addition of carboxymethyl cellulose (CMC) enhances the swelling properties. It was also found that addition of agar improves the gel strength of poly (vinyl pyrrolidone) (PVP) hydrogels but the swelling ratio reduces [8].

The biodegradable polymers, such as PVA [9], PVP are converted to CO<sub>2</sub> and H<sub>2</sub>O by digestion and degradation in the soil [10]. So, considering their environmental friendly nature such kinds of polymers have been effectively used to develop hydrogel, which can accelerate the healing of wounds [11]. Generally hydrogel contains 30-90% water that entrapped in the three dimensional network [12] structure of PVA hydrogel [11,13,14]. This large water content makes them biocompatible and is preferred as biomaterials. Even the biodegradations of such biomaterials are not affected by formed cross linked network structure [10].

Radiation is a convenient tool for modification of polymeric materials. Modification may be accomplished through cross linking, grafting and degradation. It is proved that radiation is a very suitable tool for the preparation of hydrogel especially for biomedical application [10,13]. This technology is environment friendly since

it leaves no residue or pollutants in the environment [10,15,16]. The necessary requirement to produce a usable hydrogel is the formation of cross-links between different polymer chains, resulting in a three dimensional network structure. This requirement may be achieved by the irradiation of aqueous solution of polymeric materials through gamma rays [10,13,17]. Searching for materials that have the capability to improve the properties of hydrogels is a continuous process. Regarding citric acid, they are available in citrus fruits and a good natural preservative, cleaning agent and acts as an antioxidant. When heated above 175°C, citric acid decomposes through the loss of carbon dioxide and water. Therefore, the present work was designed to carry out / investigate the effect of  $\gamma$  irradiation on the specific citric acid blend PVA hydrogel. Gel fraction, degree of swelling, water absorption (%) and water desorption (%) properties were investigated for producing medical grade wound dressing hydrogels.

## Experimental Methods

### Materials

PVA (Poly Vinyl Alcohol) is supplied by BASF, Germany and Citric acid is collected from the local market imported from Heidelberg, New York, USA.

### Preparation of PVA solution

10% PVA solution is prepared by dissolving PVA in distilled water at 600°C with continuous stirrer and keeps it for few hours.

### Preparation of citric acid solution

Various concentration of citric acid solution is prepared by dissolving citric acid in distilled water with continuous stirrer and keeps it in a water bath at 600°C for few hours and stirrer the solution after some time until the solution mixed very well.

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## Preparation of PVA/Citric acid Blend Hydrogel

At first 10% PVA is dissolve in boiled water then put into Autoclave at 121°C for 45 minutes and cooled at room temperature. After that 0.2% or 0.3% or 0.4% Citric Acid was added to the PVA solution respectively. Then 30 ml of PVA solution with citric acid was taken in glass tube of diameter 13 mm containing polythene bag then the was sealed properly.

## Irradiation of sample

Prior to irradiation the solutions were kept at room temperature for 24 hours to remove the air bubble. Irradiation was carried out by gamma rays from a Co-60 source with selected doses (10, 15, 20, 25, 30, 40, 50 and 60 kGy) at dose rate 3.54 kGy/h.

## Determination of gel fraction

The extent of cross-linking in a hydrogel is reflected by the gel fraction or content of the hydrogel. The hydrogel samples were dried in a vacuum oven to a constant weight at 60°C. The dried samples then immersed in distilled water at room temperature for 24 hours for sol extraction. The un-dissolved parts remaining in the distilled water then again dried to a constant weight at 60°C. The gel fraction was calculated as follows:

$$\text{Gel fraction (\%)} = (W_g / W_0) \times 100 \quad (1)$$

Where  $W_g$  is the weight of dry gel after extraction and  $W_0$  is the initial weight of dry gel.

## Determination of swelling ratio

Gel samples dried to a constant weight, were immersed in distilled de-ionized water at room temperature for 24 hours. The swollen sample was taken out from the water and the surface water of the sample was removed by absorbing with tissue paper. The degree of swelling was calculated as:

$$\text{Swelling ratio} = (W_s - W_0) / W_0 \quad (2)$$

Where  $W_s$  is the weight of swelled gel and  $W_0$  is the weight of dried gel after extracting sol.

## Determination of swelling ratio in NaCl solution

First irradiated samples were oven dried. Then the sols were extracted by keeping the sample in distilled water at room temperature for 24 hrs. Then the sample was again oven dried to constant weight ( $W_1$ ) and dipped in NaCl solution having different concentration for 24 hrs at room temperature. After taken out the sample from NaCl solution, the swollen sample was weighted ( $W_2$ ) after removing adhering water. The swelling ratio in NaCl solution is calculated as:

$$\text{Swelling ratio in NaCl solution} = (W_2 - W_1) / W_1 \quad (3)$$

## Determination of swelling ratio in buffer solution of different pH

First irradiated samples were oven dried. Then the sols were extracted by keeping the sample in distilled water in room temperature for 24 hrs. Then sample was again oven dried to constant weight ( $W_1$ ) and dipped in buffer solution of pH 4, 7, and 9 for 24 hrs at room temperature. After removing the adhering water, swelled sample was weighted ( $W_2$ ). The swelling is calculated as:

$$\text{Swelling ratio in buffer} = (W_2 - W_1) / W_1 \quad (4)$$

## Determination of water absorption

Gel samples were immersed in distilled water at room temperature. Gel swelled in water. Weight of swelled gel was taken after every 1 hour interval for first six hours, then at 12 hours, 18 hours and 24 hours. In each measurement, the Hydrogel surface was soaked by tissue paper and weight was taken as quickly as possible. Percent water was calculated as follows:

$$\text{Water absorption (\%)} = (W_t - W_d) / W_d \times 100 \quad (5)$$

Where  $W_t$  is the weight of the swollen gel at time  $t$  and  $W_d$  is the weight of the dry gel.

## Determination of water desorption

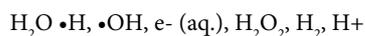
The pre weighted Hydrogel samples were placed in an open environment for water desorption and weighted at every 1 hour interval for the first six hours and then at 24, 30, 48, 72, and 96 hours. Weighting was continued until approximately constant weight was attained. Percentage of water desorption was calculated as follows:

$$\text{Water desorption (\%)} = (W_0 - W_t) / W_0 \times 100 \quad (6)$$

Where  $W_0$  is the weight of the wet Hydrogel and  $W_t$  is the weight of the Hydrogel after time,  $t$ . Room temperature and average humidity were maintained at 23-25°C and 50-55% respectively.

## Results and Discussion

The changes in gel fraction of PVA with different radiation doses and concentration of citric acid [18] are shown in Figure 1. It has been found that the gel fraction increases with radiation doses and attains maximum at 25 kGy. After this radiation dose the variation in gel fraction is not so significant. It is also found that gel fraction increases with an increase in the concentration of citric acid. Since citric acid is non-degradable organic acid in radiation, when the blend solution is subjected to radiation dose, the COOH group of citric acid cross linked with PVA monomer which causes the increase of gel content of PVA/Citric acid blend hydrogel. It has been reported that during irradiation of aqueous solution of polymeric materials the major portion of energy is absorbed for water forming free radicals and molecular products [11,13], which are shown below:



The species responsible for generating cross linking are  $\cdot OH$  and  $\cdot H$  radicals ( $G(\cdot OH) = 2.7 \times 10^{-7} \text{ mol J}^{-1}$ ,  $G(\cdot H) = 0.55 \times 10^{-7} \text{ mol J}^{-1}$ ) where the  $\cdot OH$  radical plays the major role to form cross linking (bimolecular rate constant of the order of  $10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) [13]. The radicals ( $\cdot H$ ,

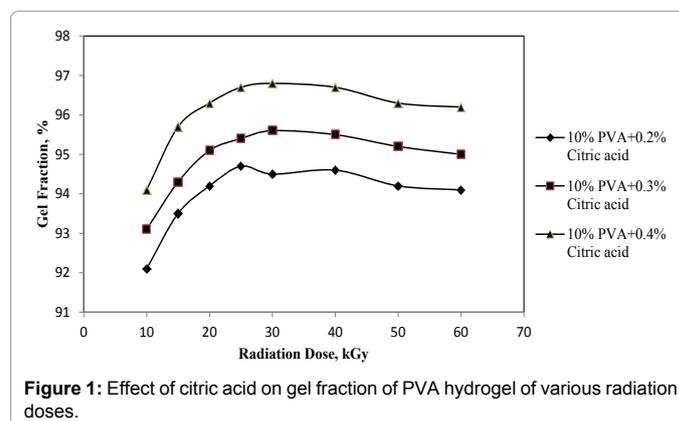


Figure 1: Effect of citric acid on gel fraction of PVA hydrogel of various radiation doses.

•OH) abstract hydrogen from the polymer chain and thus produced a carbon-centered radical in polymer chains and these carbon-centered radicals on the polymer chain further decay by forming intermolecular cross linking, results to increase in molecular weight and finally a hydrogel [13,15,16].

The changes in the swelling ratio of PVA hydrogel with different concentration of citric acid as well as radiation doses are shown in Figure 2. The swelling ratio of PVA hydrogel with citric acid decreases with an increase in radiation dose. The reduction of swelling ratio with increased radiation dose may be due to increased cross-links by the action radiation. Increased cross-links reduce the available scope of free spaces for water in the polymer network. It is also found that the swelling ratio increases with an increase in concentration of citric acid and attains maximum at 25 kGy. The water absorption capacity of this polymer is high due to the presence of -COOH group in it. It is reported that the CMC improves the swelling ratio of PVA/Sago blend Hydrogel due to the presence of the carboxyl group in the CMC molecule [7].

The changes in swelling ratio of PVA hydrogel with various concentrations of citric acid with respect to various concentration of NaCl solution at optimum Dose 25 kGy is shown in Figures 3 and 4. From figures, it is found that the swelling ratio decreases with the increase of concentration of NaCl in solution. The reduction of swelling ratio with increased NaCl concentration may be due to the increased ion concentration in the free space of the polymer network. From the above Figure 5, it is also found that swelling ratio increases with the increase of citric acid concentration on the blend hydrogel.

The changes in swelling ratio of PVA Hydrogel with various concentrations of citric acid in different pH [19] buffer solution at optimum Dose 25 kGy is shown in Figures 6 and 7. From figures, it is clear that the swelling ratio increases with the increase of pH value in the buffer solution. The increase of swelling ratio with increase in pH value may be due to the breaking of cross-links, which increases the free space of the polymer network at higher pH. From Figure 8, it is also found that swelling ratio increases with the increase of citric acid concentration on the blend hydrogel.

From Figures 9-11 shows the kinetics of water absorption in PVA hydrogel with various concentration of citric acid at different radiation doses. The amount of water absorption increases with an increase in the immersion time in water up to a constant level. From Figures 9-11, it is also seen that the amount of water absorption depends on total radiation doses. Water absorption decreases with an increase in radiation dose. This can be explained by the phenomenon that higher

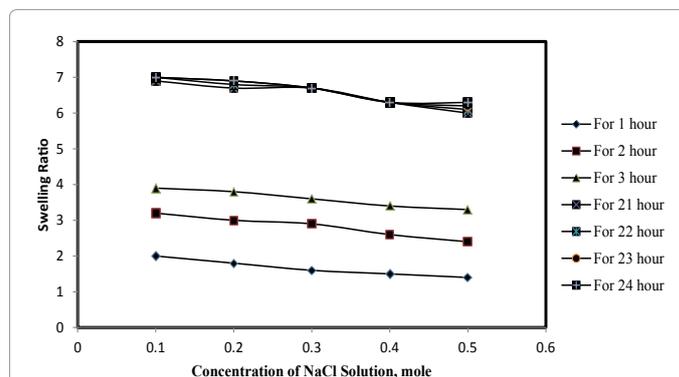


Figure 3: Effect of various concentration of NaCl solution on swelling ratio of PVA hydrogel with 0.3% citric acid at 25 kGy radiation dose.

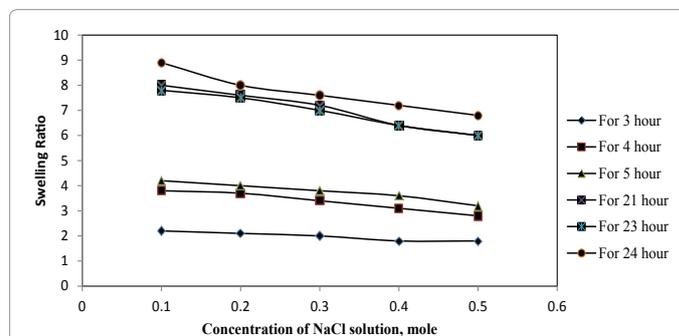


Figure 4: Effect of various concentration of NaCl solution on swelling ratio of PVA hydrogel with 0.4% citric acid at 25 kGy radiation dose.

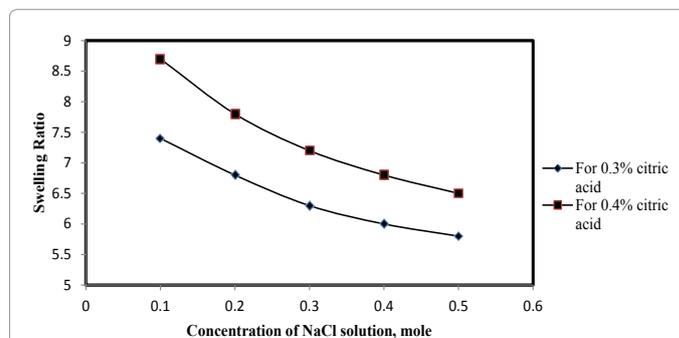


Figure 5: Effect of citric acid in various concentration of NaCl solution on swelling ratio of PVA hydrogel at 25 kGy radiation dose.

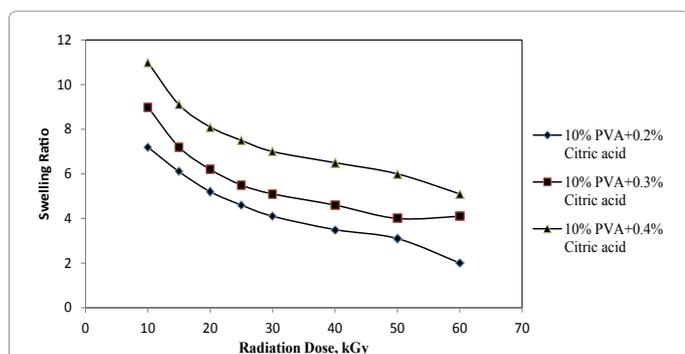


Figure 2: Effect of citric acid on swelling ratio of PVA hydrogel at various radiation doses.

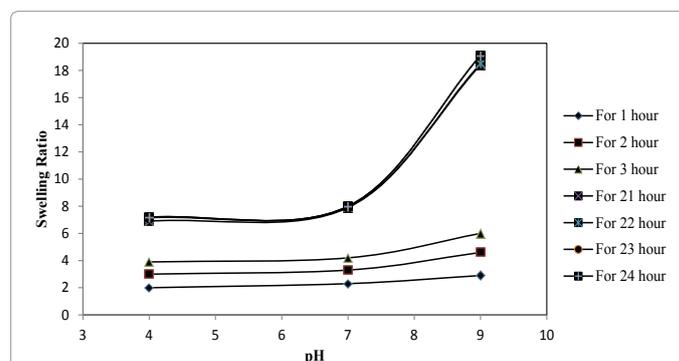
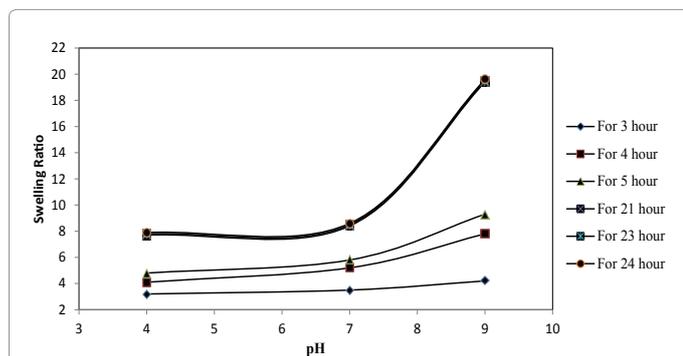
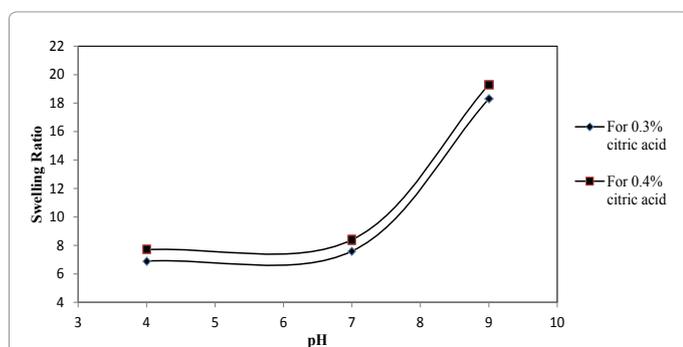


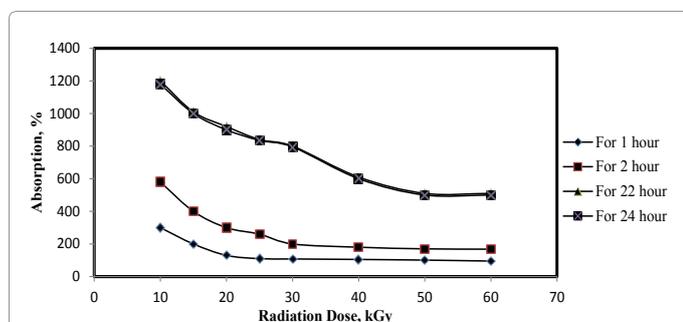
Figure 6: Effect of pH of buffer solution on swelling ratio of PVA hydrogel with 0.3% citric acid at 25 kGy radiation dose.



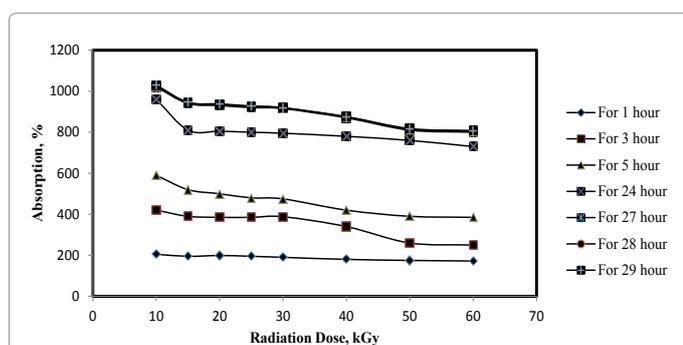
**Figure 7:** Effect of pH of buffer solution on swelling ratio of PVA hydrogel with 0.4% citric acid at 25 kGy radiation dose.



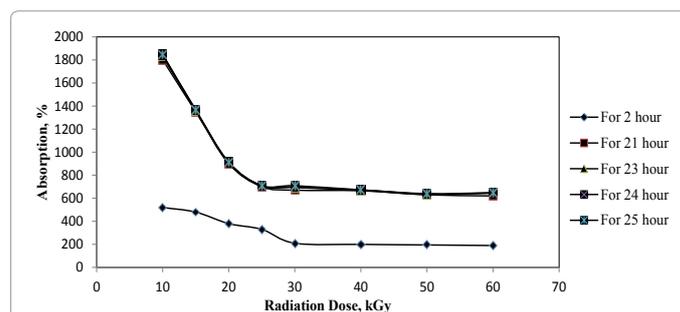
**Figure 8:** Effect of citric acid on swelling ratio of PVA hydrogel in different pH buffer solution at 25 kGy radiation dose.



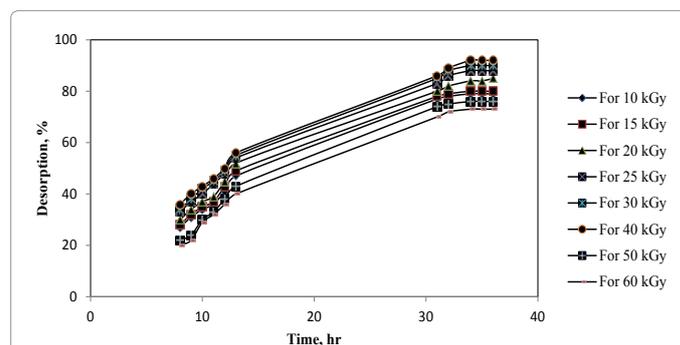
**Figure 9:** Effect of 0.2% citric acid on absorption in distilled water of PVA hydrogel at various radiation doses.



**Figure 10:** Effect of 0.3% citric acid on absorption in distilled water of PVA hydrogel at various radiation doses.



**Figure 11:** Effect of 0.4% citric acid on absorption in distilled water of PVA hydrogel at various radiation doses.



**Figure 12:** Effect of 0.4% citric acid on desorption of water of PVA hydrogel at various radiation doses.

number of cross-links, that is formed by the higher radiation doses diminished voids spaces and reduce water absorption capacity of polymer. It is also clear from the above mentioned figures that water absorption increase with increase of citric acid concentration. After 22 hr -24 hr water absorption seems to be constant.

The change of water desorption (%) of PVA hydrogel with citric acid are shown in Figure 12. From this figure it is found that the rate of desorption is very fast in first 30 hours and then attained a plateau value. The room temperature and relative humidity was maintained 23-25°C and 50%-55% respectively during the process.

## Conclusion

From the investigation of hydrogel properties, it was analyzed that the maximum gel fraction attained at 25 kGy. It was observed that the fraction increases with the increased concentration of citric acid. The swelling ratio in distilled water and water absorption decreases with the increase of radiation dose but increases with the increase in concentration of citric acid in the hydrogel. After 22-24 hr water absorption seems to be constant. At optimum radiation dose (25 kGy), NaCl solution shows an adverse effect on swelling ratio, whereas swelling ratio increases with the increase of alkalinity of solution. In case of desorption, it was found that the rate of desorption is very fast in first 30 hours and then attained a plateau value. Gel fraction, degree of swelling, water absorption (%) and water desorption (%), etc. properties revealed some sorts of applicability as medical grade wound dressing hydrogel.

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