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Studies on Swelling and Absorption Properties of the γ – Irradiated Polyvinyl Alcohol (PVA)/Kappa-Carrageenan Blend Hydrogels

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Abstract

A series of hydrogels were prepared from an aqueous mixture of Poly vinyl alcohol (PVA) and Kappa-carrageenan (KC) and irradiated the mixture at 25 kGy radiation dose with γ-radiation from 60Co γ source at room temperature (25°C). The effects of KC on the properties, such as gel fraction, swelling ratio (e.g., in distilled water, in NaCl solution with different concentration, buffer solution with different pH), water absorption, water desorption, moisture absorption and uptake of metal ion from aqueous solution of the prepared hydrogels were investigated. Incorporation of KC into the PVA obviously influences the properties of hydrogels. It is found that the gel fraction of the prepared hydrogel decreased but swelling ratio increased with increase in concentration of Kappa-carrageenan. Swelling properties in NaCl decreased with increased concentration of NaCl in aqueous solution. Swelling of the blend gel in buffer increased with the increase in pH. Water absorption properties showed that maximum absorption occurred within 24 hrs and then increasing trend of water absorption was insignificant. Water desorption is very fast upto 48 hrs and then attained a plateau value. The maximum moisture absorption occurred within 48 hrs and then the absorption was insignificant. Kappa-carragenan influences to uptake of metal (Cu^{+2}) by PVA / KC blend hydrogel with time.

Introduction

Hydrogels are two or multi component systems consisting of a three dimensional network of polymer chains and water that fills the space between macromolecules. The importance of hydrogels in biomedical applications was first realized in the late 1950s with the development of poly (2-hydroxyethyl methacrylate) (PHEMA) gels as a soft contact lens material. They are widely applicable in numerous biomedical [1] applications including ophthalmological devices, biosensors, biomembranes and carriers for controlled delivery of drugs or proteins. Although hydrogels have a number of non-biomedical applications (e.g., in agriculture), it seems that their use in the field of medicine and pharmacy is the most successful and promising [2]. Nowadays a new class of hydrogels, capable of reacting to various environmental stimuli as temperature, pH, ionic strength, solute concentration, electric field, light, sound etc., is tested for use in the so-called "intelligent biomaterials" [3].

The swollen state results from a balance between the dispersing forces acting on hydrated chains and cohesive forces that do not prevent the penetration of water into the network. Cohesive forces are most often due to covalent cross-linking [4]. Others are electrostatic, hydrophobic, or dipole-dipole in character [5]. The degree and nature of cross-linking and the crystallinity of the polymer are responsible for its characteristics in the swollen state. The ability to imbibe water and ions without the loss of shape and mechanical strength is valuable in many natural hydrogels, such as those found in muscle, tendons, cartilage, intestines, and blood.

Natural hydrogels are used in pulp and paper production, artificial silk, cellulosic membranes, and biomedical applications [6]. Synthetic hydrogels are used in prosthetic materials, soft lenses, and membranes for controlled drug release because of their compatibility with living tissue. Synthesis conditions such as temperature, monomer concentration and initiator level have significant effects on gel properties as well as impurities [7].

A simple cross-linking reaction is exemplified by polymer chains with several functional groups that are capable of reacting themselves to form chemical bonds. In principle, due to cross-linking, the polymer differs in many respects from linear and branched polymers. For example, they swell in a good solvent to form a gel but do not dissolve to form a solution. At elevated temperature, cross-linked polymers generally behave like soft but elastic solids rather than viscous liquids. Cross-linking can be carried out through the use of a cross-linking agent or by radiation energy. At some degree of conversion, the polymer chains began to form a cross-linked structure [8].

The gels are fixed to supports by coating, grafting, or chemical modification. Ion-exchange and separation membranes (qv) are hydrogels, although the term hydrogel is usually restricted to a synthetic, water-swelling polymer of soft, rubbery consistency. Its character is determined by the hydrophilic monomers and the density of the polymer network [9]. Ionogenic or charged gels [10] form a special group, with swelling and strength properties dependent on the pH of the environment.

There is a continuous search for materials that have the capability to improve the properties of the hydrogels. Kappa-carrageenan (KC) [11,12], agar [13] etc., are added to enhance the properties of poly (vinyl pyrrolidone) (PVP) hydrogel. By the addition of PVA [14] the

gel strength of PVP hydrogel is improved. Poly (vinyl alcohol) (PVA) is a hydrophilic polymer with unique properties. It absorbs water, swells easily and it has extensively been used in wound dressing. In this research work it is found the effect of γ- irradiation on swelling and absorption properties of the PVA / KC blend hydrogels.

Experimental

Materials

Poly (vinyl alcohol) (PVA), medical grade obtained from BASF, Germany was used as received and molecular weight of PVA was 145000. Kappa-carrageenan (KC), commercial grade obtained from SIGMA, USA was used to improve properties of hydrogel. Distilled water was used to prepare the sample solution.

Preparation of PVA solution without and with KC

A nine percent aqueous solution of PVA was prepared by dissolving it in distilled water. KC of different concentrations (0-4%) was added to the 9% PVA solution and treated the solution in an autoclave at 120°C for 30 minutes. Then the solution is heated in a water bath at 70°C for 1 hour. The hot solution of PVA and KC were poured into test tubes of diameter 13 mm and cooled at room temperature (22-25°C).

Irradiation of sample

The samples that were poured into test tubes were irradiated at room temperature by Co-60 γ-sources with 25 kGy radiation dose at the dose rate of 0.79 kGy/hr (Figure 1).

Preparation of dry gel sample and measurement of gel fraction

The irradiated hydrogel samples from test tubes were cut into a number of equal sized test pieces. Pieces of gel samples were dried to constant weight in a vacuum oven at 50°C. The dried samples were immersed in distilled water at room temperature for 24 hrs to remove sol fraction (water soluble parts). Then the extracted samples were dried again to a constant weight at 50°C in a vacuum oven. In this way we get dry gel. The experiment was repeated for the hydrogel prepared from different concentration of KC.

The gel fraction was calculated as follows:

Gel Fraction(%)=$W_g/W_o \times 100$

Where W_g is the weight of dry gel after extraction in water and W_o is the initial weight of dry gel.

Determination of swelling ratio in distilled water

The gel samples dried to a constant weight were again immersed in distilled water at room temperature for 24 hours. Then the samples were taken out from distilled water, surface water was removed gently by soft tissue paper and weighed. The experiment was repeated for the

Figure 1: Emission of gamma ray (γ) from an atomic nucleus.

hydrogel prepared from different concentration of KC. The Swelling ratio was calculated as follows:

Swelling ratio=W_1/W_o

where W_1 is the weight of water absorbed by the gel sample and W_o is the weight of dry gel.

Determination of swelling ratio in NaCl solution with different concentration

The gel samples dried to a constant weight were immersed in NaCl solution having different concentration (0.1, 0.3, 0.5, 0.7 and 1.0%) for 24 hours at room temperature. Then the samples were taken out from solution, surface water was removed gently by soft tissue paper and weighed. The experiment was repeated for the hydrogel prepared from different concentration of KC. The Swelling ratio in NaCl solution was calculated as follows:

Swelling ratio in NaCl Solution=W_1/W_o

where W_1 is the weight of NaCl solution absorbed by the gel sample and W_o is the weight of dry gel.

Determination of swelling ratio in buffer solution with different pH

The gel samples dried to a constant weight were immersed in buffer solution of pH 4, 7 and 9 for 24 hours at room temperature. Then the samples were taken out from solution, surface water was removed gently by soft tissue paper and weighed. The experiment was repeated for the hydrogel prepared from different concentration of KC. The Swelling ratio in buffer solution was calculated as follows:

Swelling ratio in buffer=W_1/W_o

where W_1 is the weight of buffer solution absorbed by the gel sample and W_o is the weight of dry gel.

Determination of water absorption

The gel sample dried to a constant weight was immersed in distilled water at room temperature. This sample was taken out from distilled water at different time interval (1 to 48 hours) and weighed after soaking with a soft tissue paper to remove adhering water from the surface of gel sample. The experiment was repeated for the hydrogel prepared from different concentration of KC.

The percentage of water absorption was calculated as follows:

Water absorption (%)=(W_a/W_o) $\times 100$

where W_a is the weight of water absorbed by the gel sample at time interval and W_o is the weight of dried gel.

Determination of water desorption

The pre-weighed gel samples were kept at room temperature (23-25°C) and weighed at different time interval up to 76 hours. The experiment was repeated for the hydrogel prepared from different concentration of KC. Temperature and average humidity of the experimental environment were 23-25°C and 50-55% respectively. The percentage of water desorption was calculated as follows:

Water desorption (%)=(W_d/W_i) $\times 100$

where W_d is the weight lost of gel sample after a particular time and W_i is the initial weight of hydrogel.

Determination of moisture absorption

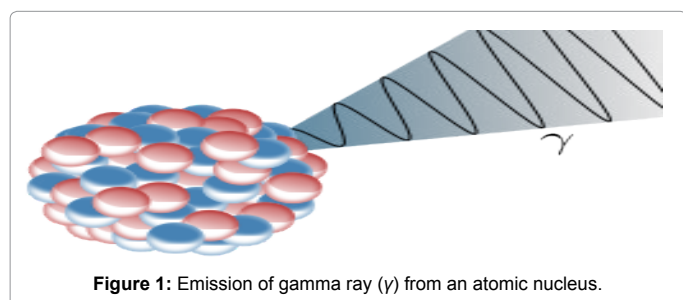The hydrogel samples were dried in oven at 50°C to a constant

weight. The dried samples were then placed in an open environment for moisture absorption and weighed at different time interval up to 76 hours. The experiment was repeated for the hydrogel prepared from different concentration of KC. Temperature and average humidity of the experimental environment were 23-25°C and 50-55% respectively. The percentage of moisture absorption was calculated as follows:

Moisture absorption (%)=$(W_{ma}/W_{i0}) \times 100$

where W_{ma} is the weight of gel sample after a particular time and W_{i0} is the initial weight of dry gel sample.

Determination of uptake of metal ion (Cu^{+2})

Apparatus:

1. Spectrophotometer, Wavelength 435 mm, matched absorption cell 10 to 15 mm.

2. Separating funnel.

Reagents:

1. Zinc diethyldithiocarbamate: Dissolve 1 gm of sodium diethyldithiocarbamate in 100 ml water and 2 gm of $ZnSO_4$. Extract the resulting Zinc diethyldithiocarbamate by shaking with 100 ml $CHCl_3$ and separate the chloroform solution. Dilute to 1 litre. Store in amber colored bottle. This reagent is stable for at least six months.

2. Copper Standard Solution: 0.393 gm of copper sulphate pentahydrate ($CuSO_4 \cdot 5H_2O$) is taken into a small beaker and dissolve in water. Then 3 ml conc. H_2SO_4 is added and transfer in a 1000 ml volumetric flask and make up to the mark (100 ppm). From this solution 10 ml is taken in a 100 ml volumetric flask and added water up to the mark. This solution is 10 ppm (0.01 mg of Cu per milliliter or 10 microgram per gram).

Procedure: The gel samples dried to a constant weight were immersed in Copper solution at room temperature. These samples were taken out from Copper solutions at different time intervals (1 to 48 hours). The aqueous solution is then shaken with a solution in chloroform diethyldithiocarbamate to form and extract the yellow copper complex and optical density is measured by using spectrophotometer at wavelength 435 mm. in respect of a blank solution.

Preparation of calibration curve: 1, 3, 5, 7 and 10 ml solution is taken individually in five small beakers from the 10 ppm of standard solution of $CuSO_4 \cdot 5H_2O$ and made to 40 ml each by adding water. Take this solution in separating funnel and added 25 ml Zinc diethyldithiocarbamate in chloroform and shaked for 2 min. and separated chloroform layer and optical density is measured by using spectrophotometer at wavelength 435 mm. in respect of a blank solution (Figure 2).

Results and Discussion

Gel fraction of PVA/KC blend hydrogel

The gel is the insoluble part of a cross-linked polymer. It is measured after removing the sol (soluble portion) in a suitable solvent. The gel content (%) of Poly (vinyl alcohol) (PVA) / Kappa-carrageenan (KC) blend hydrogel prepared by γ-radiation at 25 kGy dose and different concentrations of KC are determined by gravimetric procedure.

From the Figure 3, it is found that the gel content of PVA / KC blend hydrogel is decreased with increase in concentration of KC. This is occurred by the reason that KC is a radiation degradable polymer, when PVA with KC is subjected to radiation dose, KC degraded to low molecular weight compounds that causes the reduction of the gel fraction of PVA hydrogel with KC due to the degraded KC molecules may prevent to cross-link of PVA molecules [1]. The cross-link density in PVA/sago and PVP/sago blend hydrogels decreases due to degradation of sago by radiation [15]. Starch also reduces the gel content of PVA/starch blend hydrogel [16].

Swelling ratio of PVA/KC blend hydrogel in distilled water

Swelling ratio reflects the cross-linking of a polymer. The changes of swelling ratio of hydrogel without and with various concentration of Kappa-carrageenan are shown in the Figure 4.

Swelling is a result of the balance between two forces. One is osmotic force due to covalent or non covalent bond in the gel and another force is dispersing force. Osmotic force pushes water into polymer network. Whereas dispersing force exerted by polymer chains resists it. So with the increase of cross-link density a limited scope is available for free water enters into the vacant spaces of cross-link network.

From the Figure 4, it is shown that the degree of swelling increases with increase in concentration of the Kappa-carrageenan. The swelling ratio increases from 16.15 to 20.49 for the concentration of KC from 0.0% to 4.0% at the radiation dose of 25 kGy. Kappa-carrageenan is an anionic polymer. The water absorption capacity of kappa-carrageenan molecule is high due to the presence of strong hydrophilic group, $-OSO_3^-$ [17]. As a result, the swelling ratio of PVA/KC blend hydrogel is increased with increase in concentration of Kappa-carrageenan.

Swelling ratio of PVA/KC blend hydrogel in NaCl Solution

The degree of swelling for a hydrogel at equilibrium is characteristics of the polymer composition and cross-linking density, the temperature, P^H and ionic strength of the medium in which the gel is stored and the
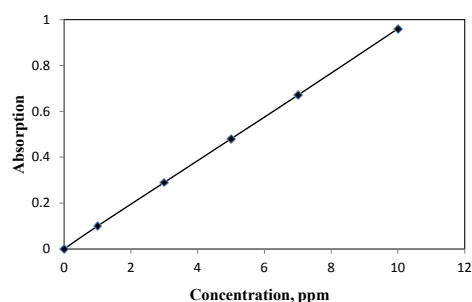
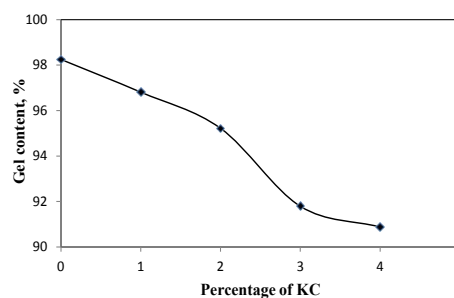**Figure 2:** Calibration curve for uptake of metal concentration.

Figure 3: Effect of concentration of KC on the gel content for 9% PVA / KC blend hydrogel.

existing hydrostatic pressure. The degree of swelling can be altered by some environmental factors. Adding some an electrolyte can change the swelling ratio.

From the Figure 5 it is observed that swelling ratio in NaCl solution is lower than that of distilled water. Swelling ratio decreases with the increased the concentration of NaCl in aqueous solution. This is due to the fact that the concentration of counter ions increases, the effective ionization of the polymer is reduced and the electrostatic free energy of the system decreases. There is a reduction of volume i. e. shrinkage of the gel material. So the swelling ratio decreases with the increase concentration of the NaCl solution. It is also found from Figure 4 that the swelling ratio increases with increase in concentration of the kappa-carrageenan in PVA / KC blend hydrogel.

Swelling ratio of PVA/KC blend hydrogel in buffer solution

The first responsive gel was a pH sensitive gel made from poly (methacrylic acid) described by Katchalsky in 1949. This gel absorbed hundred times of its dry weight in water at high pH but shrink progressively as the pH was reduced. Figure 6 represents the effect of pH on the swelling ratio of polyvinyl alcohol/ kappacarragenan blend hydrogel.

From the Figure 6 it is found that the swelling ratio increases with the increase in pH. The lower swelling ratio in acidic region may be due to protonation and thereby resisting the association of water through hydrogen bonding. The increasing in the pH value of buffer, the deprotonation may be occurred and increases the swelling ratio.

From the Figure 6 it is found that the swelling ratio also increases with increasing of the concentration of Kappa-carrageenan. This may be happened due to reduction of cross-linking and increased the presence of $-OSO_3^-$ group with increase in concentration of KC in PVA / KC blend hydrogel.

Water absorption (%)

Water absorption is a measurement of swelling. The changes of water absorption (%) of PVA hydrogel without and with various concentrations of KC as well as different times are shown in the Figure 7.

It is found from the Figure 7 that the absorption of water of the hydrogel increases with time and increases with the increase of Kappa-carragenan ratio in the blend gel. It is also found that maximum absorption occurs within 24 hours of dipping in water. Then the absorption of water is insignificant.

Water desorption (%)

The changes of water desorption (%) of PVA hydrogel without and with various concentrations of KC as well as different times are shown in the Figure 8.

It is found from the Figure 8 that the desorption of water of the blend gel increases with time but decreases with the increase of Kappa-carragenan ratio in the blend gel. This decrease in the water desorption may be due to the formation of more cross linked density in the hydrogel as increase PVA concentration cause increase cross linking in the PVA network. It is also found that maximum desorption occurs within 48 hours in normal environmental condition. Then the desorption of water is insignificant.

Moisture absorption (%)

The changes of moisture absorption (%) of PVA hydrogel without and with various concentrations of KC as well as different times are shown in the Figure 9.
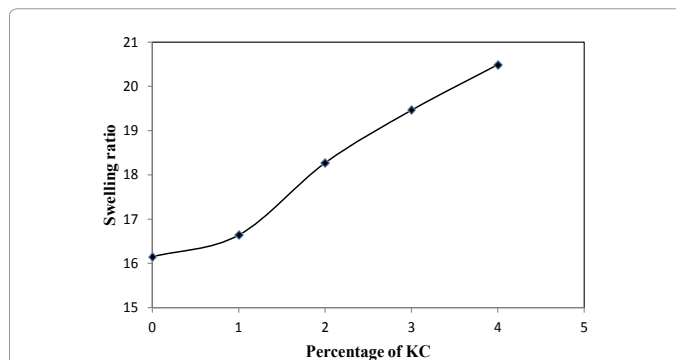

Figure 4: Degree of swelling in water with different concentration of KC in 9% PVA / KC blend hydrogel.
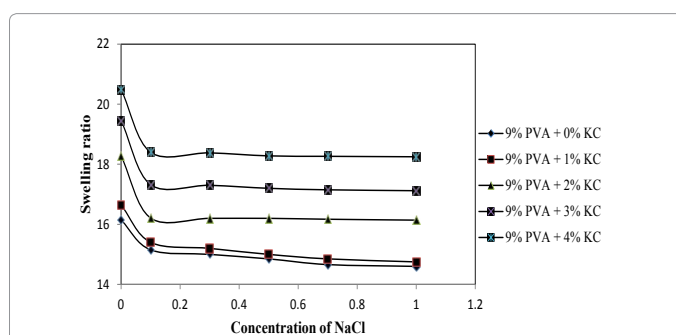

Figure 5: Effect of the concentration of KC on the ionic strength of NaCl solution on the swelling ratio of PVA / KC blend hydrogel.
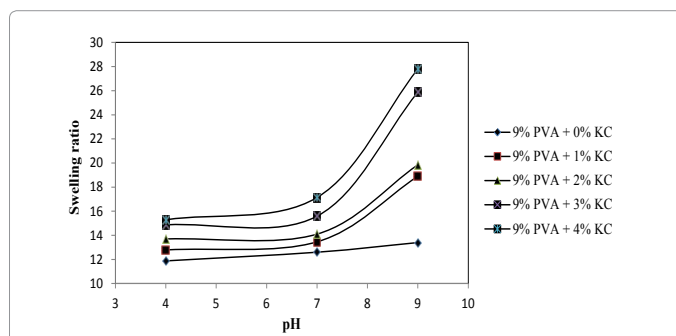

Figure 6: Effect of the concentration of KC on the swelling ratio of the PVA / KC blend hydrogel with different pH.
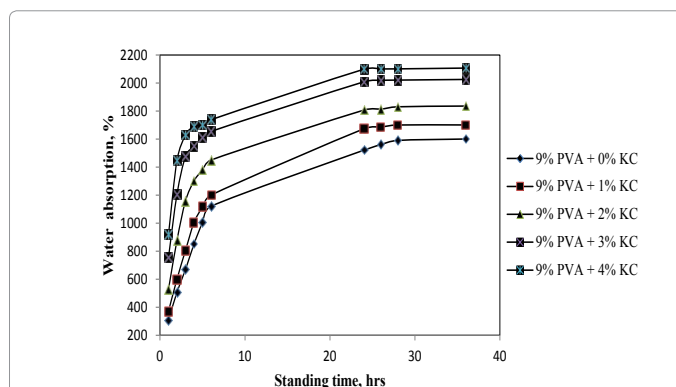

Figure 7: Effect of Kappa-carragenan ratio on the water absorption of PVA / KC blend hydrogel prepared at 25 kGy.

It is found from the Figure 9 that the absorption of moisture of the blend gel increases with time and increases with the decrease of Kappa-carragenan ratio in the blend gel. It is also found that maximum absorption occurs within 48 hours and then the absorption of moisture is insignificant.

Uptake of metal (Cu^{+2}) by PVA / KC blend hydrogel

The changes of uptake of metal (Cu^{+2}) of PVA hydrogel without and with various concentrations of KC as well as different times are shown in the Figure 10.

It is found from the Figure 10 that metal uptake capacity of PVA / KC blend hydrogel increases with time and maximum uptake occurs within 24 hours and then the uptake of metal (Cu^{+2}) is insignificant. It is also found that metal uptake capacity of PVA / KC blend hydrogel increases with increasing concentration of KC. This may be due to increase the content of strong hydrophilic group, -OSO$_3^-$ with increase KC in the blend hydrogel.

From the research work it is found that swelling and absorption properties of Poly vinyl alcohol (PVA) / Kappa-carragenan (KC) blend

Figure 8: Effect of Kappa-carragenan ratio on the desorption in the PVA / KC blend hydrogel prepared at 25 kGy.

Figure 9: Effect of Kappa-carragenan ratio on the absorption in the PVA/KC blend hydrogel prepared at 25 kGy.

Figure 10: Effect of concentration of KC on the uptake of metal (Cu^{+2}), with PVA and KC blend hydrogel.

hydrogel prepared at 25 kGy increased with increase in concentration of KC. Since KC is a radiation degradable polymer, when PVA with KC is subjected to a radiation dose, KC degrades to a low molecular weight compound. The degraded KC molecules may prevent to cross-link of PVA molecules and may cause the reduction of the gel content of PVA hydrogel with increased concentration of KC. Again swelling and water absorption properties are increased with the decreased in gel content of hydrogel. Finally required properties are enhanced with the use of KC.

Conclusion

Poly vinyl alcohol (PVA) is a cross linked polymer as it forms gel when subjected to radiation. The gel fractions of the Poly vinyl alcohol (PVA) hydrogel and Poly vinyl alcohol (PVA)/Kappa-carragenan (KC) blend hydrogel increases with increased concentration of KC but it never become 100%. The gel fraction of PVA hydrogel is higher than that of PVA/KC blend hydrogel and with the increase of KC concentration in the blend hydrogel the gel fraction decreases. The swelling ratio in distilled water of PVA is higher than that of PVA/KC blend hydrogel and with the increase KC concentration the degree of swelling decreases. The metal ion (Cu^{+2}) uptake capacity increases with the increased concentration of KC in the PVA/KC blend hydrogel. The metal ion (Cu^{+2}) uptake properties showed that maximum uptake occurred within the first 24 hours and then the uptake is insignificant. PVA/KC blend hydrogel can be used for water purification because of its uptake capacity of metal ion from aqueous solution as well as for biomedical applications such as all types of wound dressing and covers can act also as slow-release drugs.

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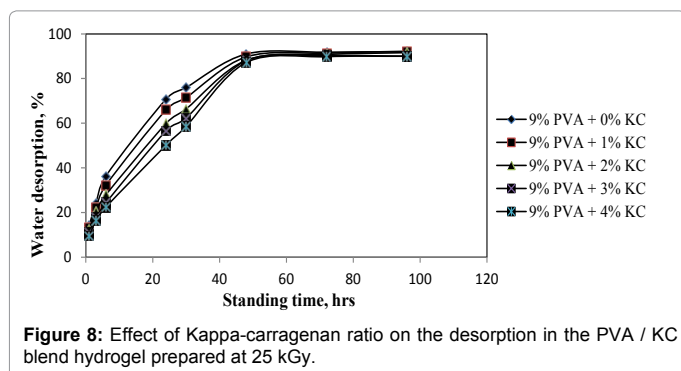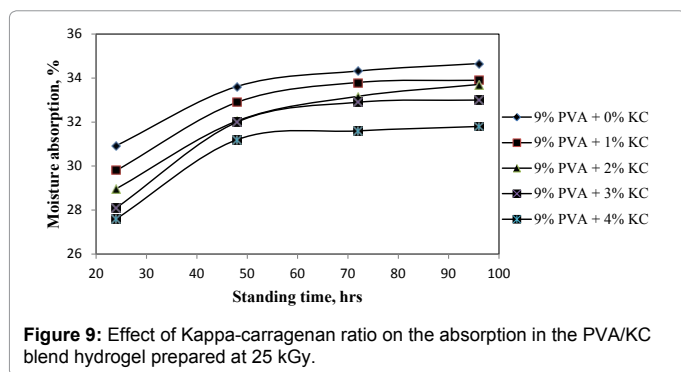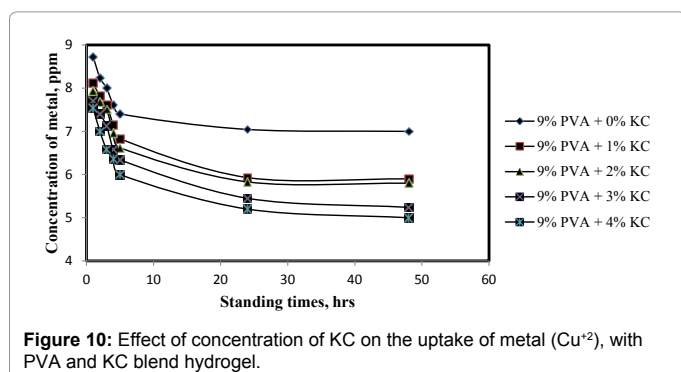
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