Chapter Three
Methodology

Materials & method:

2.1 Materials:

- PVA (polyvinyl alcohol) $(CH_2CHOH)_n$, SIGMA (Mw = 72,000 g/mol, 99 – 100% hydrolyzed) & Cu_2O (Sigma - USA): polymer binder/plasticizer and available in the form of powders, fibers and films.
- Optical densitometer & UV-visible spectrophotometer model Camspec M530 - USA
- Syringe 20 ml & Magnetic stirrer/with control temp (60 – 80 C^o) (Herenz - German)
- Petri dish & Sealed black envelopes (Herenz - German)

2.2Method:

PVA as 5% has been dissolved in distill water under control temp of 80 ˚C, with continuous stirring using magnetic stirrer for 3 hours, after obtaining homogenous solution and cooled to ambient temperature; a cuprous oxide Cu_2O with an amount of 0.5 grams were added to the solution (500 ml of PVA) and stirred for two hours. The solution has been poured in petri dishes; each contains 20ml using Syringe. The petri dish with solution left under ambient temperature and controlled area free of dust, and light for 3 days for water vaporization (dryness). Then casted films have been peeled off from petri dishes, cut into small pieces 2×2 cm, packaged in small fastened envelopes, sandwiched between 0.5 cm buildup polystyrene for electronic range accumulation at films then irradiated with γ-ray from ^{60}Co teletherapy machine receiving doses (0, 1, 2, 4, 6,.. 12 Gy).

The ^{60}Co-teletherapy machine calibrated based on IAEA report standard series No. 16, (2000) & Andreo et al, (2004). Then the films characterized by using optical densitometer and UV spectroscope to show the induced optical effects. The collected data analyzed in forms of spectrum and correlation using EXCELL software 2010.

3.1 Materials and equipment:

3.1.1 Polyvinyl alcohol (PVA)

Poly (vinyl alcohol) is an important material in view of its large-scale applications, such as biomaterials, biosensors, electrochemical sensors, membranes with selective permittivity viscous medium for controlling the crystallization process of salts, for controlled drug delivery or catalytic systems, etc. because it is a non-toxic, non-carcinogenic, biodegradable, biocompatible water-soluble and non-expensive polymer. It could also be matrix for metal ions or salts in ecological composites (C.A.Finch et al., 1973). PVC can react with different organic or inorganic substances, via OH groups from its macromolecular chain and three dimensional networks, which can absorb very high water content (up to 1800%). .

PVA is one of the important polymer binder and available in the form of powders, fibers and films. It can be obtained from poly (vinyl acetate) (PVAc) by esterification and has distinct crystallinity. The polymer has intermolecular chin of 2.5 Ǻ and consists of 13 glycol linkages, in which all hydroxyl groups are arranged along the same side of the chain (Sakurada, 1985). These in turn account for the mechanical strength and strong interactions between different chains. The unit cell of PVA consists of two monomer units of vinyl alcohol (CH_2CHOH) (Bunn, 1948) as in Figure 3.1.

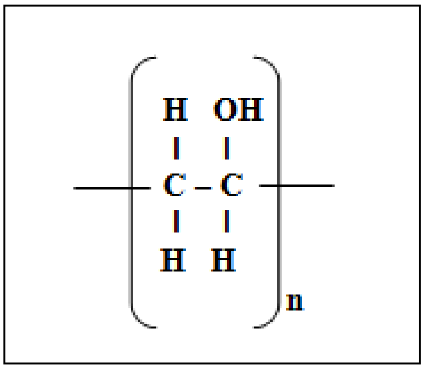

Figure 3.1 Chemical structure of poly (vinyl alcohol) (PVA) monomer.

PVA is glassy and does not dissolve in water at room temperature unless the ester groups of PVAc are cleaved to a hydroxyl content of 87-89%. It dissolves easily at temperature above glass-transition temperature, T_g ranging from 60 to 90 ^oC. It is non-ionic vinyl polymer, tough with film forming capacity due to hydrogen bonding (Ravve, 2000), fibres and tubes forming capability and highly resistant to hydrocarbon solvents (Molyneux, 1983). It is highly resistive to electrical conductivity with low dielectric loss. Its electrical conductivity and charge storage capability can be significantly influence by doping with suitable impurities (Nagaraja, *et al.*, 2002). Due to biocompatibility, PVA has been used in medical devises, materials for drug delivery system, carrier for cell signaling, sizing, adhesives, emulsification and bio-separation membranes (Yano, *et al.*, 2003).

3.1.2 Cuprous oxide (Cu_2O):

is an oxide of copper found in nature as cuprite and formed on copper by heat; used chiefly as a pigment and as a fungicide. Also known as cuprous oxide. It is used as an antifouling agent for marine paints as an alternative of Tributyltin compounds. It can be formed by heating copper in air at around 300 - 800°C: ... For laboratory uses, pure copper (II) oxide is better prepared by heating copper (II) nitrate,copper (II) hydroxide or copper(II) carbonate:

$2\ Cu(NO_3)_2 \rightarrow 2\ CuO + 4\ NO_2 + O$. $Cu(OH)_2\ (s) \rightarrow CuO\ (s) + H_2O\ (l)$

cuprous oxide is a chemical compound with a chemical formula (Cu_2O) shown in Figure 3.2

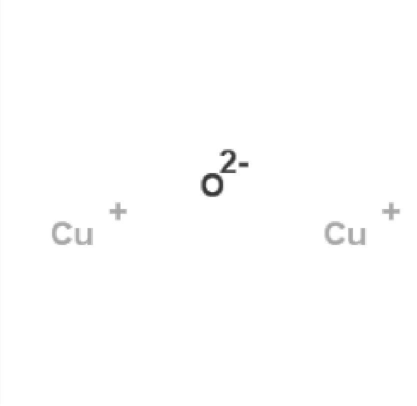

Figure 3.2 The chemical structure of the Cuprous oxide compound.

3.1.2 ^{60}Co teletherapy unit:

3.1.3 The source

The ^{60}Co source is produced by irradiating ordinary stable ^{59}Co with neutron in a reactor. The nuclear reaction can be represented by ^{59}Co (n , γ) ^{60}Co.

The ^{60}Co source, usually in the form of a solid cylinder disc or pallets, is contained inside stainless capsule and sealed by welding. The double welded seal is necessary to prevent any leakage of the radioactive material. The ^{60}Co source decay to ^{60}Ni with the emission of β particles (E_{max} = 0.32 Mev) and two photons per disintegration of energies 1.17 and 1.33 Mev, these two photons constitute the useful treatment beam. The β particles are absorbed in the cobalt metal and the stainless-steel capsules resulting in the emission of bremstrung x-ray and small amount of characteristic x-ray.

A typical teletherapy^{60}Co source is a cylinder of diameter ranging from 1.0 to 2.0 cm and is positioned in the cobalt unit with its circular end facing the patient. The fact that the radiation source is not a point source complicates the beam geometry and gives rise to what is known as the geometric penumbra.

3.1.5 Source Housing

The housing for the source is called the source head. It consists of a steel shell filled with lead for shielding purposes and a device for bringing the source in front of an opening in the head from which the useful beam emerges. Also, a heavy metal alloy sleeve is provided to form an additional primary shield when the source is in the off position. A number of methods have been developed for moving the source from the off position to the on position. These methods have been discussed in detail by Johns and Cunningham (10). It will suffice here to mention briefly four different mechanisms: (a) the source mounted on a rotating wheel inside the source head to carry the source from the off position to the on position; (b) the source mounted on a heavy metal drawer plus its ability to slide horizontally through a hole running through the source head-in the ON position the source faces the aperture for the treatment beam and in the OFF position the source moves to its shielded location and a light source mounted on the same drawer occupies the on position of the source; (c) mercury is allowed to flow into the space immediately below the source to shut off the beam; and (d) the source is fixed in front of the aperture and the beam *can* be turned on and off by a shutter consisting of heavy metal jaws. All of the above mechanisms incorporate a safety feature in which the source is returned automatically to the off position in case of a power failure.

Fig. 3.3 shown the cobalt-60 machine that used to irradiate the films

3.1.6 Beam Collimation

A collimator system is designed to vary the size and shape of the beam to meet the individual treatment requirements. The simplest form of a continuously adjustable diaphragm consists of two pairs of heavy metal blocks. Each pair can be moved independently to obtain a square or a rectangle-shaped field. Some collimators are multivane type, i.e. multiple blocks to control the size of the beam.

3.1.7 UV-Visible spectroscopy:

The UV visible spectroscopy version and model (Camspec M350) used in this research as shown in Figure (3.4)

Figure (3.4) The UV visible spectroscopy version and model (Camspec M350) used in this research

3.1.8 Optical densitometer:

The optical densitometer is a simple device that shines white light onto one side of the developed film and electronically measures the amount of light reaching the other side. The optical densitometer has a small sensitive area (aperture), typically about 3 mm in diameter, and measurements of OD correspond to that specific area of the film. If the intensity of the light measured with no film in the optical densitometer is given by I_0, and the intensity measured at a particular location ona film is given by I, then the *transmittance* (T) of the film at that location and the OD are defined as follows:

$$T = I/I_0 \qquad (3.1)$$

$$OD = -\log_{10}(T) = \log_{10}(1/T) = \log_{10}(I_0/I) \qquad (3.2)$$

If the transmission through the film is $T = 0.1 = 10^{-1}$, then OD = 1; if the transmission is $T = 0.01 = 10^{-2}$, then OD = 2. The relationship between OD and T is analogous to that between pH and the hydrogen ion concentration (pH = -

10glO [H30+]). The inverse relationship is $T = 10^{OD}$.The optical densitometer that we used in this work is from PTW model densix as shown in Figure (3.5).

Figure (3.5) Optical densitometer that we used in this work is from PTW model densix.

3.1.9 TLD reader:

The thermoluminescent dosimeter, or TLD, is a type of radiation dosimeter. A TLD measures ionizing radiation exposure by measuring the intensity of visible light emitted from a crystal in the detector when the crystal is heated. The intensity of light emitted is dependent upon the radiation exposure. Materials exhibiting thermoluminescence in response to ionizing radiation include but are not limited to calcium fluoride, lithium fluoride, calcium sulfate, lithium borate, calcium borate, potassium bromide and feldspar.

The two most common types of TLDs are calcium fluoride and lithium fluoride, with one or more impurities to produce trap states for energetic electrons. The former is used to record gamma exposure, the latter for gamma and neutron exposure (indirectly, using the Li-6 (n,alpha) nuclear reaction; for this reason, LiF dosimeters may be enriched in lithium-6 to enhance this effect or enriched in lithium-7 to reduce it). As the radiation interacts with the crystal it causes electrons in the crystal's atoms to jump to higher energy states, where they stay trapped due to intentionally introduced impurities (usually manganese or magnesium) in the crystal, until heated.

Heating the crystal causes the electrons to drop back to their ground state, releasing a photon of energy equal to the energy difference between the trap state and the ground state. The electrons can also drop back to ground state after a long period of time; this effect is called *fading* and is dependent on the incident radiation energy and intrinsic properties of the TLD material. As a result, each material possesses a limited shelf life after which dosimetric information can no longer be obtained. This varies from several weeks in calcium fluoride to up to two years.

It can be used both for environmental monitoring and for staff personnel in facilities involving radiation exposure, among other applications. The TLD reader sued in this research was PCL3 from PTW, The PCL3 is an automatic reader to measure accumulated dose signals from thermo luminescent dosimeters. Up to 80 detectors can be evaluated in one cycle. The detectors are stored in a magazine, automatically processed and loaded into a second magazine. TL chips of 4.5 mm diameter and 0.8 mm thickness and TL powder are preferably used, alternatively TL rods and TL films are suitable. The detectors are heated by contact. The heating temperature of maximum 600 °C is controlled automatically with an accuracy of better than 1%. The measuring range covers seven decades with a linear response of up to 12 Gy using standard TLD material and up to 500 Gy using material LiF:Mg,Ti. The background reading is corrected automatically before starting each measurement. An internal reference light provides for automatic calibration of the photomultiplier. The dose reading can be calibrated in the radiation units Gy, Sv, rem or rad or in the unit C (electrical charge). The PCL3 system is prepared for TLD evaluation under nitrogen atmosphere. The modular cabinet design of the device presents very easy access to the mechanical and electronic components for maintenance and repair. A computer software for control and evaluation is included in the standard package.

Figure 3.6 shown the TLD reader system (PCL3 from PTW) used in this research

3.2 Method:

3.2.1 Preparations of PVA/ (Cu_2O) composite sample films

The PVA-stabilized Cu2O particles were prepared using a novel and simple rout in aqueous medium at room temperature under aerobic conditions. Initially, Cu(II) ions were fixed in PVA matrix via complex formation with OH groups, subsequently this PVA–Cu(II) macromolecular complex as a precursor reacted with ascorbic acid as a reducing agent at pH = 12 to obtain the PVA–Cu2O composite. The products were characterized using XRD ,FESEM, FTIR, and UV–Visible techniques. The as-prepared PVA–Cu2O composite was applied as an effective and recyclable heterogeneous catalyst for 1,3-dipolar cyclo addition reactions between terminal alkynes and azides to prepare 1,2,3-triazoles under an environmentally friendly reaction conditions. The substituted triazoles were produced of various aryl and benzyl azides using a catalytic amount of this composite as efficient, stable, and air- and moisture-tolerant catalyst in excellent yields in water at room temperature. These PVA-stabilized Cu2O particles could be recovered in a facile manner from the reaction mixture and reused several times without any loss of catalytic activity.

The PVA stock was supplied by SIGMA (Mw = 143.09 g/mole, 99 – 100% hydrolyzed). The PVA solutions were made by dissolving 3.00 g PVA powder in 100 ml distilled water at temperature of 80 ^{o}C on a beaker. The solution was magnetically stirred throughout at that temperature for 3 hours and then left to cool at room temperature.

After cooling to room temperature, we took the PVA solution into dark room and hybridized with 0.2 wt% of Cu2O and stirred for 2h. Then the PVA / Cu2O solution poured in a petri-dish to form films by casting method in dark room. Then the PVA/ Cu2O blend solution was divided into two, 40 ml each (The remaining 20 ml evaporated due to heat) and spread into a specially made glass caster, 10 cm in diameter and left to dry at ambient temperature in dark room for at least 3 days to remove water. Then films will be peeled off the petri-dish, cut into small films 2x2cm, loaded in sealed dark plastic packs (dental film envelope).

3.2.2 Irradiation of film samples

All film samples together with TLD were irradiated with doses in range of 0 – 12 Gy, using ^{60}Co γ-rays irradiation facility, from the radiotherapy department in King Fahad Medical City, Riyadh–Saudi Arabia as shown in Figure (3.8).

The samples stick at the Perspex phantom, the films were embedded at right angle to direction of the radiation beam.

The dose rate on the exact date of measurement January 12, 2016 was 1.35 Gy/min. The new dose rate was calculated based on the half-life, $T_{1/2}$, of the source, i.e. the elapsed time in which the activity of the source reduced by half, is equal to 5.27 years by the equation (3.3)

$$\dot{D} = \dot{D}_0 \exp(-\ln 2\ t / T_{1/2}) \tag{3.3}$$

Where $\dot{D}_0$ is the dose rate at time $t = 0$