1.1 Hydrogels:

Hydrogels are hydrophilic polymeric networks that can imbibe a large amount of biological fluids including water and can swell several times their dry volume. Hydrogels have attracted tremendous research interest over many years, in part for fundamental reasons and in part because of the potential for a wide range of applications. Their ability to absorb water in large amount is due to the presence of hydrophilic functional groups such as -OH, -CONH-, CONH₂, -COOH, and -SO₃H in their networks. To qualify a polymer as hydrogel, in practical sense, the dry material should spontaneously imbibe about twenty times its own weight of aqueous fluid. While undergoing this phenomenon of volume change of 2000 percent, the swelling material retains its original identity [1].

The first generation of hydrogels with swelling capacity up to 40-50% appeared in the late 1950s and were mainly based on polymers derived from hydroxyalkyl methacrylate and related monomers. These hydrogels were used in developing contact lenses which marked a revolution in ophthalmology. The need to improve these lenses, and the emerging of other medical problems resulted in the development of a second generation of hydrogels with swelling degrees of 70-80% which widened the scope of their application.

Hydrogels are most commonly obtained by free radical crosslinking polymerizations of hydrophilic acrylate or methacrylate monomers with small quantities of crosslinking agents containing two (or more) polymerizable double bonds. Examples of typical crosslinking agents include N,N¹ methylenebisacrylamide, triallylamine, ethylene glycoldiacrylate, tetraethyleneglycoldiacrylate, trimethylolpropane-triacrylate and the methacrylate analogs of the aforementioned acrylates. Hydrophilic esters of acrylic or methacrylic acid (such as 2-hydroxyethyl methacrylate and its analogs) have been
extensively polymerized using the above reagents to form hydrogels which typically exhibited a maximum swelling of 40-50 wt% water. The unique set of properties exhibited by the hydroxyethyl(meth)acrylate hydrogels have lead to their extensive application in a host of biomedical materials and devices.

Hydrogels can also be designed with controllable responses so as to shrink or expand with changes in external environmental conditions [1]. The extent of swelling or de-swelling in response to the changes with external environment of the hydrogel could be so drastic that the phenomenon is referred to as volume collapse or phase transition [2-3]. Hydrogels may respond uniquely to changes in external environmental conditions such as ionic strength [4], electromagnetic radiation [5], pH [3-7], and temperature [8,9,10-12]. These conditions can be applied individually or in combinations and altered as desired. Other important conditions such as the type of salt used for the preparation of buffer [13-14], the solvent used as the medium [15], photoelectric stimulus [16] and the external stress [17-18] also influences on the hydrogel’s performance. These unique properties make hydrogels as excellent candidates for numerous applications in biomedical, antimicrobial, pharmaceutical, agricultural and consumer-oriented fields [1].

1.1.1. Applications of Hydrogels

Hydrogels are used in many potential applications due to their excellent high water absorbency, water retention and environmental sensitive nature. These hydrogels are widely used in many products such as disposable diapers, feminine napkins, soil for agriculture and horticulture, gel actuators, water-blocking tapes for biomedical applications, and as absorbent pads. Some of the applications of hydrogels are described below.
1.1.2 Agricultural and Horticulture Applications

Hydrogels have been commonly utilized in agricultural field mainly as water storage granules [19]. The need to improve the physical properties of soil to increase the productivity in the agricultural sector was visualized in 1950s [20]. This led to the development of water-soluble polymers such as PVA, PEG and PAM to function as soil conditioners [20] followed by the introduction of water-swelling polymeric hydrogels in the early 1980s [21]. Water-swelling hydrogels from crosslinked PAM, crosslinked polyacrylates and copolymers of acrylamide and acrylates for such applications have been reported [21].

Soils containing moist hydrogels act as conditioners and increases water-holding capacity of the potting media by 50 to 100%. The increased water supply enhances the germination process by reducing the relative amount of water loss via evaporation and drainage. Swellable hydrogel delivery systems are also commonly utilized for controlled release of agrochemicals and nutrients of importance in agricultural applications to enhance the plant growth with reduced environmental pollution. A number of researchers have reported the versatility of polymeric hydrogels in agricultural applications [21, 22].

1.1.3. Hydrogels used as feminine napkins and baby diapers

Polymeric hydrogels are expanding into many product areas. Personal hygiene products, however, use more than 95% of the 350,000 metric tons of hydrogels manufactured per year in the world. The principal use in disposable diapers is due to their thinner capacity by the introduction of hydrogel polymers. The polymer absorbs liquid that
was held previously in open spaces between the fibers of cellulose fluff. The cores of early polymer containing diapers contained about 12% superabsorbent polymer. Current diapers are designed to incorporate up to 60% of superabsorbent polymer in addition to thinner size of diapers for infants, and also the superabsorbent polymers are used in feminine napkins.

**1.1.4. Hydrogels used in construction materials**

Other applications are being developed based on the capacity of these polymers to absorb water and salt solutions. For example leaking of water is often a problem in major construction projects. A sealing composite that swells slightly in water can be prepared by blending the hydrogel with rubber. Because of the incompatibility of the rubber and the hydrogel polymer, appropriate modification of the interface of the polymer phase is critical to the success of this material. The sealing composite is used between the concrete blocks for the construction of walls. When water contacts the composite, the sealant swells slightly, making an impermeable barrier for further penetration of water. Such a composite was used in the construction of the Channel linking England to France [23].

**1.1.5. Hydrogels used in water blocking tapes**

Leaking of water is also detrimental to the performance of fiber optic communication cables and power transmission cables. Water-blocking tapes prevent intrusion of water [24]. The tape is prepared by applying a dispersion of hydrogel in a polymeric binder onto a nonwoven fabric which provides flexibility. Because of the cables exposed either to seawater or ground water containing divalent cations, superabsorbents incorporating sulfonate functional groups rather than carboxylic acid groups are preferred for this application [25].
1.1.6. Hydrogels used in vegetable and fruit storage buildings

At high humidity, hydrogel absorbs and releases moisture more effectively than silica gel[23]. This property can be used for example, to prevent damage from moisture condensation on walls and ceilings in humid buildings. Since powdered products are difficult to apply in such cases, sheets and fibers have been developed. Simple laminates of polymer hydrogels are incorporated between two tissue layers as absorbent pads for meat and poultry packages. Sheets are made by polymerizing monomers directly onto nonwoven fabrics. These are used in vegetable and fruit storage buildings to maintain a constant humidity and to prevent spotting of the produce caused by dripping of the condensed water from surface of the structure [23].

1.1.7. Artificial snow

Artificial snow made up with hydrogel is used in an indoor ski center near Tokyo. The snow is made by swelling the polymer with 100 times its mass of water and freezing it in a place with the cooling system. The frozen gel layer is groomed to yield snow with a realistic feel, similar to powder snow [26]. By using these polymers, the temperature of the air in the building can be at least 10 °C higher than with conventional artificial snow, increasing comfort for the skiers.

1.1.8. Gel actuators and Sensors

Gel actuators are an active area of research related to hydrogels; these materials are used as artificial “muscles” in robots to provide motion to mimic human musculature. Variation of the swelling conditions is used to control the actuator. For example, changing the temperature, light intensity, electric field strength, or composition (pH, salt
concentration) of the swelling fluid can change the extent of swelling and cause the gel to move in response to the change in volume [27].

1.1.9. Medical Waste Treatment

Hydrogels are widely used in medical waste management. They can solidify the waste fluids and retain it even under significant pressure. This solidification of medical waste has lots of advantages to the end user such as reduction in biohazard handling, ease of disposal and cost saving. Also hydrogels have an application in hot and cold pads. When used in wound dressing it absorbs blood and exudates that enabling a clean and hygienic dressing [1, 28].

1.1.10. Hydrogels in Biomedical applications

Hydrogels due to their special properties like higher water content, nontoxicity, biocompatibility, being soft, elastic, pH responsive, temperature responsive, stimulative nature and environmental sensitive, are used in many biomedical applications.

The biomedical applications of hydrogels can be classified into three distinct categories namely, coatings such as catheters, homogeneous materials such as contact lenses and devices such as sustained drug delivery systems [2, 28].

**Coatings:** Sutures, Catheters, Intra Uterine Devices (IUD’s), Blood detoxicants, Sensors, Vascular grafts, Electrophoresis cells and Cell structure substrates.

**Homogeneous Materials:** Electrophoresis gels, Contact lenses, Artificial corneas, Vitreous-humour replacements, Oestrous –Induces, Soft tissue substitutes, Burn dressings, Bone in growth sponges, Dentures, Ear drum plugs, Synthetic cartilage’s, Hemodialysis membranes.

**Devices:** Enzyme therapeutic systems, artificial organs, Sustained drug delivery systems.
1.1.11. Other applications of Hydrogels

Hydrogels are used as thickening agents (e.g., starch and gelatin) in foods. The addition of hydrogel-forming agents to incontinence products increases the fluid uptake and ensures improved retention capacity. Hydrogels are used in photographic technology because they are light permeable and can also store light sensitive substances. In electrophoresis and chromatography, the separation and diffusion characteristics of the gel structure are exploited. Hydrogels, thus applied, operate within only a very limited range of swelling.

1.2 Nanocomposite polymer hydrogels

The term “nanocomposite” is commonly used for filled polymers containing dispersed nanofillers with average particle sizes smaller than 100 nm [29]. In the past decades, metal nanoparticles have been extensively investigated for their unique properties and for providing important building blocks for the construction of functional structures [30]. Incorporating them into polymeric matrices has been proved to be an effective method to enhance the functions of the polymeric materials [31]. These metal nanoparticle (MNP)/polymer nanocomposite materials exhibited novel combination properties of metal nanoparticles and polymers that were attractive for the potential applications in catalysis, optics, electronics, sensor and biomedicine [32]. MNP s can be obtained by various synthetic routes, such as electrochemical methods, decomposition of organometallic precursors, reduction of metal salts in the presence of suitable (monomeric or polymeric) stabilizers, or vapour deposition methods [33]. Sometimes, the presence of stabilizers is required to prevent the agglomeration of nanoclusters by providing a steric
and/or electrostatic barrier between particles and, in addition, the stabilizers play a crucial role in controlling both the size and shape of nanoparticles.

In this sense, the development of polymer-stabilized MNPs (PSMNPs) is considered to be one of the most promising solutions to the MNPs stability problem[34-35]. For this reason, the incorporation of MNPs into polymeric matrices has drawn a great deal of attention within the last decade as polymer-metal nanocomposites. The main advantage of the nanocomposite ion exchange materials is the location of metal nanoparticles near the surface of the polymer what substantially enhances the efficiency of their biocide and catalytic application [36].

1.3 Metal nanocomposites for anti microbial applications

The fundamental knowledge on the preparation and nature of metal–polymer nanocomposites has a long history that is connected to the names of many famous scientists. The oldest technique for the preparation of metal–polymer nanocomposites that can be found in the literature was described in an abstract that appeared in 1835[37]. In an aqueous solution, a gold salt was reduced in the presence of gum arabic, and subsequently a nanocomposite material was obtained in the form of a purple solid simply by coprecipitation with ethanol. Around 1900, widely forgotten reports describe the preparation of polymer nanocomposites with uniaxially oriented inorganic particles and their remarkable optical properties. Dichroic plants and animal fibrils (e.g., linen, cotton, spruce, or chitin others) were prepared by impregnation with solutions of silver nitrate, silver acetate, or gold chloride, followed by reduction of the corresponding metal ions under the action of light. During the last three decades, dichroic fibers were prepared with many different metals (i.e., Pd, Pt, Cu, Ag, Au, Hg, etc.)[37].
Nano-sized metal particles such as silver, gold, and copper are highly toxic to microorganisms [39-42], exhibiting strong biocidal effects on as many as 16 species of bacteria including *Escherichia coli* [43]. Nanoparticles have an extremely large relative surface area, thus increasing their contact with bacteria or fungi, and vastly improving their bactericidal and fungicidal effectiveness. Silver nanoparticles show excellent antimicrobial activity by binding both to microbial DNA, preventing bacterial replication, and to the sulfhydryl(-SH) groups of the metabolic enzymes of the bacterial electron transport chain causing their inactivation [44,45].

Nanosilver particles have been applied to a wide range of healthcare products such as burn dressings, scaffold, skin donor and recipient sites, water purification systems, and medical devices [46–51]. Multipurpose systems are required to exhibit superior antibacterial activity toward germs on contact without releasing any toxic biocides. Ongoing research efforts, on three dimensional network hydrogels, suggest that huge free space available between the cross-linked networks in the swollen stage behaves as nanoreactors for generating the nanoparticles[52]. These hydrogel nanoreactors offer a platform for nucleation and growth of nanocrystals, which eventually lead to nanoparticle formation. Further, gel–nanoparticle systems have opened a new skylight for different applications in biomedical engineering and these approaches are most effective and safe because they are compatible with most of biological molecules, cells, tissues, etc [53].

**1.4 Advantages of Au nanoparticles as contrast agents in biomedicine**

Colloidal Au nanoparticles with strong surface-plasmon-enhanced absorption and scattering are an important addition to the toolbox of imaging labels and contrast
agents[54-60]. Au nanoparticles are not susceptible to photo bleaching and they appear biocompatible and noncytotoxic, as supported by recent experiments on human cells[61]. Further, colloidal Au has been used as a radioactive label \textit{in vivo} since the 1950s [62].

\textbf{1.5. Objectives of the Present Investigation}

In view of the wide range of applications of MNPs, the primary objective of this investigation is to synthesize bimetallic nanoparticles of controllable size and that are embedded in polymer hydrogel networks for various biomedical applications. This can be achieved by entrapment of Ag,Cu,Au nanoparticles in biopolymers such as gelatin and chitosan.

The objectives of this investigation are.

- To develop novel hydrogel metal nanocomposites using synthetic and natural polymers.
- To develop hydrogel monometallic and Bimetallic nanocomposites
- Particle size analysis of the nanoparticles as well as the hydrogel metal and bimetallic nanocomposites
- Swelling studies of the hydrogel metal bimetallic nanoparticles in different media
- To enhance the antibacterial properties using metal nanocomposites and compare the enhanced antibacterial property with bimetallic nanocomposites
1.6 References:


1 Introduction to Hydrogels


1 Introduction to Hydrogels


1 Introduction to Hydrogels


Diego, (1989) 1
