"STUDIES ON MODIFIED HYDROGELS OF ACRYLAMIDE COPOLYMERISED WITH NATURAL RESOURCES"

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Dedicated To
My Parents

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CERTIFICATE

This is to certify that the dissertation entitled "STUDIES ON MODIFIED HYDROGELS OF ACRYLAMIDE COPOLYMERISED WITH NATURAL RESOURCES" submitted by Mr. Devendra Pratap Dwivedi to Delhi College of Engineering in Applied Chemistry and Polymer Technology is a record of bonafide work carried out by him. Mr.Devendra Pratap Dwivedi has worked under our guidance and supervision for fulfilled the requirement for the submission of this dissertation.

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ABSTRACT

Hydrogels were prepared by copolymerisation of Acrylamide with natural resources ; (1) Cane sugar juice (2) Sapodilla (chikoo- Manilkara zapota) extract (3) Pineapple(Ananas comosus) juice with the help of initiator [(Potassium Peroxydisulphate).(KPS-$K_2S_2O_8$)]and using N,N'-Methylenebisacrylamide (N,N-MBAAm) as crosslinking material in aqueous medium. Hydrogels of homopolymer of acrylamide and its copolymers with acrylic acid and methacrylic acid were also prepared for the purpose of comparision of results obtained. These hydrogels were characterised by FTIR ,SEM and XRD analysis . Swelling study of the above hydrogels were performed in aqueous media as a function of time. Stimuli response of pH of medium and temperature on swelling were also studied . Hydrogels were used for sorption study of hazardous metal ions [Hg(II) , Pb(II) , Cd(II)] as a function of Time , pH and temperature .

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CHAPTER 1

What is Hydrogel?

INTRODUCTION & LITERATURE REVIEW

1

1.1.Gel:

A **gel** is a solid, jelly-like material that can have properties ranging from soft and weak to hard and tough. Gels are defined as a substantially dilute cross-linked system, which exhibits no flow when in the steady-state.[1] By weight, gels are mostly liquid, yet they behave like solids due to a three-dimensional cross-linked network within the liquid. It is the crosslinks within the fluid that give a gel its structure (hardness) and contribute to stickiness (tack). In this way gels are a dispersion of molecules of a liquid within a solid in which the solid is the continuous phase and the liquid is the discontinuous phase

Composition:

Gels consist of a solid three-dimensional network that spans the volume of a liquid medium and ensnares it through surface tension effects. This internal network structure may result from physical bonds (**physical gels**) or chemical bonds (**chemical gels**), as well as crystallites or other junctions that remain **intact** within the extending fluid. Virtually any fluid can be used as an extender including water (hydrogels), oil, and air (aerogel) . Both by weight and volume, gels are mostly fluid in composition and thus exhibit densities similar to those of their constituent liquids. Edible jelly is a common example of a hydrogel and has approximately the density of water

Types of gels:

1.1.1.Hydrogels:

Hydrogel (also called aquagel) is a network of polymer chains that are hydrophilic, sometimes found as a colloidal gel in which water is the dispersion medium. Hydrogels are highly absorbent (they can contain over 99% water) natural or synthetic polymers. Hydrogels also possess a degree of flexibility very similar to natural tissue, due to their significant water content.

Common uses for hydrogels include:

1.Currently used as scaffolds in tissue engineering. When used as scaffolds, hydrogels may contain human cells to repair tissue. 2.Environmentally sensitive hydrogels which are also known as 'Smart Gels' or 'Intelligent Gels'. These hydrogels have the ability to sense changes of pH, temperature, or the concentration of metabolite and release their load as result of such a change. 3.As sustained-release drug delivery systems. 4.Provide absorption, desloughing and debriding of necrotic and fibrotic tissue. 5.Hydrogels that are responsive to specific molecules, such as glucose or antigens, can be used as biosensors, as well as in DDS. 6.Used in disposable diapers where they absorb urine, or in sanitary napkins.
7.Contact lenses (silicone hydrogels, polyacrylamides) 8.EEG and ECG medical electrodes using hydrogels composed of cross-linked polymers (polyethylene oxide and polyAMPS and polyvinylpyrrolidone) 9.Water gel explosives 10.Rectal drug delivery and diagnosis

Other, less common uses include:

Breast implants, Granules for holding soil moisture in arid areas ,Dressings for healing of burn or other hard-to-heal wounds. Wound gels are excellent

for helping to create or maintain a moist environment. Reservoirs in topical drug delivery; particularly ionic drugs, delivered by iontophoresis

Common ingredients are e.g. polyvinyl alcohol, sodium polyacrylate, acrylate polymers and copolymers with an abundance of hydrophilic groups.

Natural hydrogel materials are being investigated for tissue engineering; these materials include agarose, methylcellulose, hyaluronan and other naturally derived polymers.

1.1.2.Organogels:

An **organogel** is a non-crystalline, non-glassy (thermoplastic) solid material composed of a liquid organic phase entrapped in a three-dimensionally cross-linked network.

The liquid can be, for example, an organic solvent, mineral oil, or vegetable oil. The solubility and particle dimensions of the structurant are important characteristics for the elastic properties and firmness of the organogel. Often, these systems are based on self-assembly of the structurant molecules.[2,3]

Organogels have potential for use in a number of applications, such as in pharmaceuticals,[4] cosmetics, art conservation,[5] and food.[6] An example of formation of an undesired thermoreversible network is the occurrence of wax crystallization in petroleum.[7]

1.1.3.Xerogels:

A **xerogel** is a solid formed from a gel by drying with unhindered shrinkage. Xerogels usually retain high porosity (25%) and enormous surface area (150–900 m^2/g), along with very small pore size (1-10 nm). When solvent removal occurs under hypercritical (supercritical) conditions, the network does not shrink and a highly porous, low-density material known as an *aerogel* is produced.

Heat treatment of a xerogel at elevated temperature produces viscous sintering (shrinkage of the xerogel due to a small amount of viscous flow and effectively transforms the porous gel into a dense glass.

1.2.Hydrogels(in Detail):

Hydrogels are polymeric networks those imbibe large quantity of water without dissolving themselves. Hydrogels contain water solubiliging groups such as –OH , -COOH , $-NH_2$, $CONH_2$ and $–SO_3H$.

These polymers are insoluble in water due to presence of three-diamensional network. In the equilibrium swollen state there exists a balance between dispersive and cohesive forces . Cohesive forces are due to covalent crosslinking [8] , electrostatic , hydrophobic or dipole – dipole interactions[9,10] . In the swollen state of hydrogel , characteristic properties depend upon degree and nature of crosslinking and tacticity and crystallinity of polymer .

Hydrogels may or may not have ordered structure , however , structure of ordered hydrogels resemble hydrogel of biological systems and they are highly reaction specific and exhibit superior biocompatibility [11] .

Natural hydrogel such as those found in muscles , tendons ,cartilage ,intestines and blood have ability to imbibe water without loss of shape or mechanical strength [12] .

1.2.1.Classification of Hydrogel:

Hydrogels may be of natural origin or prepared by copolymerisation of two monomers or with some natural polymers like starch , cellulose or gelatin with suitable monomer . These are classified with respect to their origin , composition and mode of synthesis [13-16]

1.2.1.1.Classification based on preparation method:

Homopolymer hydrogels (one type of hydrophilic mer). Copolymer hydrogels (two types of mers, at least one hydrophilic). Multipolymer hydrogels (more than three types of mers). Interpenetrating polymeric hydrogels (swelling a network of polmer1 in mer2, making intermeshing network of polymer1 and polymer2 [17]

1.2.1.2.Classification based on ionic charges:

Neutral hydrogels, Anionic hydrogels,Cationic hydrogels, Ampholytic hydrogels

1.2.1.3.Classification based on structure:

Amorphous hydrogels (chains randomly arranged), Semicrystalline hydrogels (dense regions of ordered macromolecules, i.e. crystallites) ,Hydrogen-bonded hydrogels

1.2.1.4.Classification based on stimuli response: (INTELLIGENT OR SMART HYDROGELS)

1.2.1.5.Classification based on crosslinking(Chemically crosslinked and Physically crosslinked., described in chapter 2)

1.2.1.6.Classification based on origin:

1.2.a.Homopolymer hydrogels[18]and Co polymer hydrogels:

1.2.a.1.Poly(vinyl alcohol):

A hydrophilic polymer ; poly(vinyl alcohol) (PVA) is a material that holds tremendous promise as a biological drug delivery device because it is nontoxic, hydrophilic, and exhibits good mucoadhesive properties . The linear PVA chains are cross-linked using glyoxal, glutaraldehyde, or borate. and semicrystalline gels were prepared by exposing aqueous solutions of PVA to repeating freezing and thawing by Peppas and Hassan (2000) . Structure cross-linked with the quasi-permanent crystallites. Peppas method is the preferred method for preparation as it allows for the formation of an “ultrapure” network without the use of toxic cross-linking agents. Ficek and Peppas (1993) used PVA gels for the release of bovine serum albumin using novel PVA microparticles.

1.2.a.2.Poly(ethylene glycol):

Hydrogels of poly(ethylene oxide) (PEO) and poly(ethylene glycol) (PEG) are used in biomedical applications . Three preparation techniques are used for cross-linked PEG networks: (i) chemical cross-linking between PEG chains,
(ii) radiation cross-linking of PEG chains, and (iii) chemical reaction of mono- and difunctional PEGs. Stringer and Peppas (1996) have prepared PEO hydrogels by radiation cross-linking . It is safe as no toxic cross-linking agents are required.
Additionally, they investigated the diffusional behaviour of smaller molecular weight drugs, such as theophylline, in these gels.

1.2.b.Hydrogel Based on Acrylic Acid ,Acrylic Esters and substituted methacrylates or Acrylates:

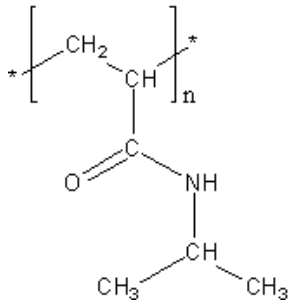
Above monomers in presence of cross linkers mostly bifunctional ethylene dimethacrylates (EDMA) and 3-oxopentamethylene dimethacrylates (DEGDMA) or trifunctional crosslinking agents such as trimethlolpropanetrimethacrylate (TPT) are also used to get desirable gels [19].The most commonly used hydrogel of this class is poly(2-Hydroxyethylmehacrylate) ,poly(HEMA) [20,21] .It highly stable to hydrolysis because of ester bond [22].However its only disadvantage is its friable nature .However if HEMA is crosslinked with ethylene diacrylate it gives pliable , soft xerogels and hydrogels [23] .Properties of poly(HEMA) can be modified by crosslinking but very low network density is responsible for poor mechanical strength[14] and swelling [24].
Strength can be increased by incorporation of hydroxypropylmethacrylate (HPMA) into the network .Swellability of HEMA can be increased by crosslinking with higher di hydroxy alcohols and DEGDMA and 3,6,9-trioxaundecamethylene dimethacrylates (TEGDMA)[19].Hydrogels of HEMA with superior mechanical and tensile strength can be obtained by copolymerisation with hydrophobic comonomers [25].

1.2.c.Hydrogel Based on Acrylamide and substituted Acrylamide:

A **Polyacrylamide Gel** is a separation matrix used in electrophoresis of biomolecules, such as proteins or DNA fragments. Here electrophoresis means applying an electric field to mediate the movement of particles through the polyacrylamide gel. Acrylamide monomers undergo radical polymerisation with crosslinking agents to form hydrogels .A Am hydrogels are crosslinked by N,N-methylene bisacrylamide (N,N-MBAAm). These hydrogels have sufficient hydrophilicity but are low in hydrolytic stability and tensile strength .

Radiation induced crosslinking of AAm and Acrylic Acid forms transparent hydrogel useful for coating catheters ,surgical sutures ,and antifogging films .

1.2.c.1.Poly(N-isopropylacrylamide):

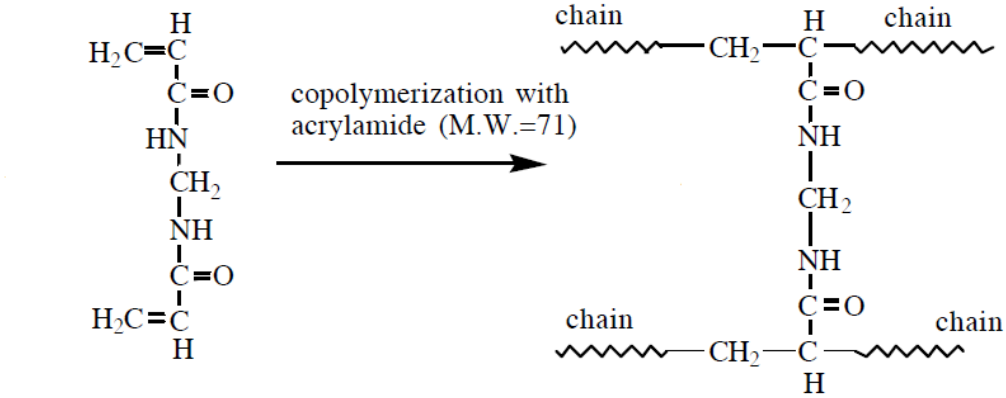


Chemical structure of poly(*N*-isopropylacrylamide)

Poly(*N*-isopropylacrylamide) is a temperature-responsive polymer that was first synthesized in the 1950s.[26]

It forms a three-dimensional hydrogel when crosslinked with *N,N'*-methylene-bis-acrylamide (MBAm) or *N,N'*-cystamine-bis-acrylamide (CBAm).

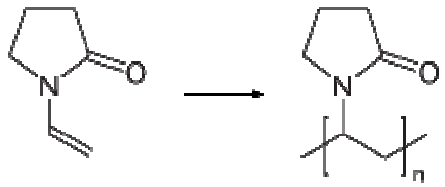
Crosslinking of Acrylamide(25.1)



"bis" Monomer (M.W.= 154)

1.2.c.2.Polyvinylpyrrolidone

Polyvinylpyrrolidone (**PVP**), also commonly called Polyvidone or Povidone, is a water-soluble polymer made from the monomer *N*-vinylpyrrolidone:(27)
PVP is soluble in water and other polar solvents. When dry it is a light flaky powder, which readily absorbs up to 40% of its weight in atmospheric water. In solution, it has excellent wetting properties and readily forms films.
This makes it good as a coating or an additive to coatings. PVP was first synthesized by **Prof. Walter Reppe**. PVP was initially used as a blood plasma substitute and later in a wide variety of applications in medicine, pharmacy, cosmetics and industrial production.(28)



N-2-Vinyl-2-pyrrolidone(NVP) **Polyvinylpyrrolidone (PVP)**

It is used as a binder in many pharmaceutical tablets;[29] it simply passes through the body when taken orally. However, autopsies have found that crospovidone does contribute to pulmonary vascular injury in substance abusers who have injected pharmaceutical tablets intended for oral consumption.[30] .PVP added to iodine forms a complex called povidone-iodine that possesses disinfectant properties.[31] This complex is used in various products like solutions, ointment, pessaries, liquid soaps and surgical scrubs. It is known for instance under the trade name Betadine .It is used in pleurodesis (fusion of the pleura because of incessant pleural effusions). For this purpose, povidone iodine is equally effective and safe as talc, and may be preferred because of easy availability and low cost.[32]

PVP is also used in many technical applications:

As adhesive in glue stick and hot melts ,as special additive for batteries, ceramics, fiberglass, inks, inkjet paper and in the chemical-mechanical planarization process ,as emulsifier and disintegrant for solution polymerization ,

As photoresist for cathode ray tubes (CRT) ,use in aqueous metal quenching ,for production of membranes, such as dialysis and water purification filters ,as a binder and complexation agent in agro applications such as crop protection, seed treatment and coating ,as a thickening agent in tooth whitening gels[33] , as an aid for increasing the solubility of drugs in liquid and semi-liquid dosage forms (syrups, soft gelatine capsules) and as an inhibitor of recrystallisation ,as an additive to Doro's RNA extraction buffer and as an liquid-phase dispersion enhancing agent in DOSY NMR [34]

PVP is also used in personal care products, such as shampoos and toothpastes, in paints, and adhesives that must be moistened, such as old-style postage stamps and envelopes. It has also been used in contact lens solutions and in steel-quenching solutions.[35,36] PVP is the basis of the early formulas for hair sprays and hair gels, and still continues to be a component of some.

As a food additive, PVP is a stabilizer. It is also used in the wine industry as a fining agent for white wine. Other references state that polyvinyl pyrrolidone and its derivatives are fully from mineral synthetic[37] origin. Therefore, its use in the production should not be a problem for vegans.

In molecular biology, PVP can be used as a blocking agent during Southern blot analysis as a component of Denhardt's buffer. It is also exceptionally good at absorbing polyphenols during DNA purification.

In microscopy, PVP is useful for making an aqueous mounting medium.[38]

1.2.d.INTELLIGENT OR SMART HYDROGELS[18]:

Hydrogels may exhibit swelling behavior dependent on the external environment. Environmentally responsive materials show drastic changes in their swelling ratio due to changes in their external pH, temperature, ionic strength, nature

and composition of the swelling agent, enzymatic or chemical reaction, and electrical or magnetic stimuli (Peppas, 1993). The ability of pH- or temperature-responsive gels to exhibit rapid changes in their swelling behavior and pore structure in response to changes in environmental conditions lend these materials favourable characteristics as carriers for bioactive agents, including peptides and proteins. This type of behavior may allow these materials to serve as self-regulated, pulsatile drug delivery systems.

1.2.d.1.pH-Sensitive Hydrogels:

These hydrogels are swollen ionic networks containing either acidic or basic pendant groups. In aqueous media of appropriate pH and ionic strength, the pendant groups can ionize developing fixed charges on the gel. All ionic materials exhibit a pH and ionic strength sensitivity.

The mesh size of the polymeric networks can change significantly with small pH changes. These gels typically contain side ionisable side groups such as carboxylic acids or amine groups.

The most commonly studied ionic polymers include poly(acrylamide) (PAAm), poly(acrylic acid) (PAA), poly(methacrylic acid) (PMAA), poly(diethylaminoethyl methacrylate) (PDEAEMA), and poly(dimethylaminoethyl methacrylate) (PDMAEMA). The swelling and release characteristics of anionic copolymers of PMAA and PHEMA (PHEMA-*co*-MAA) have been investigated.

In acidic media, the gels did not swell significantly; however, in neutral or basic media, the gels swelled to a high degree because of ionization of the pendant acid group. Brannon-Peppas and Peppas (1991) have also studied the oscillatory swelling behavior of these gels.

1.2.d.2.Temperature Sensitive Hydrogels:

Temperature-sensitive polymers typically exhibit a lower critical solution temperature (LCST), below which the polymer is soluble.

Above this temperature, the polymers are typically hydrophobic and do not swell significantly in water (Kim, 1996). However, below the LCST, the crosslinked gel swells to significantly higher degrees because of the increased compatibility with water. Cross-linked poly(*N*-isopropyl acrylamide) (PNIPAAm) is prepared having LCST 34.3◦C. Below this temperature, significant gel swelling occurred. The transition about this point was reversible. The transition temperature can be raised by copolymerizing PNIPAAm with small amounts of ionic monomers. Dong and Hoffman (1991) prepared heterogeneous gels containing PNIPAAm that collapsed at significantly faster rates than homopolymers of PNIPAAm. Yoshida *et al*. (1995) and Kaneko *et al*. (1996) developed an ingenious method to prepare comb-type graft hydrogels of PNIPAAm. The main chain of the cross-linked PNIPAAm contained small-molecular-weight grafts of PNIPAAm. Under conditions of gel collapse (above rapid collapse. These materials had the ability to collapse from a fully swollen conformation in less than 20 minutes, whereas comparable gels that did not contain graft chains required up to a month to fully collapse. Such systems show major promise for rapid and abrupt or oscillatory release of drugs, peptides, or proteins.

1.2.d.3.Complexing Hydrogels:

Some hydrogels may exhibit environmental sensitivity due to the formation of polymer complexes. Polymer complexes are insoluble, macromolecular structures formed by the noncovalent association of polymers with affinity for one another. The complexes form as a result of the association of repeating units on different chains (interpolymer complexes) or on separate regions of the same chain (intrapolymer complexes). Polymer complexes are classified by the nature of the association ; as stereocomplexes, polyelectrolyte complexes, or hydrogen-bonded complexes. The stability of the associations is dependent on such factors as the nature of the swelling agent, temperature, type of dissolution medium, pH and ionic strength, network composition and structure, and length of the interacting polymer chains.

In this type of gel, complex formation results in the formation of physical cross-links in the gel. As the degree of effective cross-linking is increased, the network mesh size and degree of swelling is significantly reduced. As a result, if hydrogels are used as drug carriers, the rate of drug release will decrease dramatically upon the formation of interpolymer complexes. Bell and Peppas (1995) have discussed a class of graft copolymer gels of PMAA grafted with PEG, poly(MAA-*g*-EG).

These gels exhibited pH-dependent swelling behavior due to the presence of acidic pendant groups and the formation of interpolymer complexes between the ether groups on the graft chains and protonated pendant groups. In these covalently cross-linked, complexing poly(MAA-*g*-EG) hydrogels, complexation resulted in the formation of temporary physical cross-links due to hydrogen bonding between the PEG grafts and the PMAA pendant groups.

The physical cross-links were reversible in nature and dependent on the pH and ionic strength of the environment. As a result, these complexing hydrogels exhibit drastic changes in their mesh size in response to small changes of pH. Promising new methods for the delivery of chemotherapeutic agents using hydrogels have been recently reported.

Novel biorecognizable sugar-containing copolymers have been investigated for the use in targeted delivery of anti-cancer drugs.

Peterson *et al*. (1996) have used poly(*N*-2-hydroxypropyl methacrylamide) carriers for the treatment of ovarian cancer.

1.2.e.Hydrogels based on origin[39]:

1.2.e.1.Hydrogels based on natural polymers:

Natural biodegradable polymers, such as hyaluronic Acid, fibrin , collagen , gelatin (produced by partial hydrolysis of collagen) , and chondroitin sulphate, have inherent biocompatibility and induce specific cell-material interactions. Other polysaccharides such as alginate, dextran, chitosan, and pullulan have also often been applied. Many of these polymers are biocompatible and depending on their molecular weight they may be excreted by the kidneys. Structural elements of several important polysaccharides are shown in Figure (b). Peptide sequences, synthesized by solid-phase peptide synthesis or by genetic engineering, are increasingly used as components for the preparation of hydrogels. Peptides used for the preparation of hydrogels can perform a specific function, such as crosslinking, cell adhesion,

enzymatic degradation and heparin binding. The main drawback of these peptide containing biomaterials is their time-consuming and costly synthesis.

1.2.e.2.Hydrogels based on synthetic materials:

The most commonly used synthetic hydrogels are based on poly(ethylene glycol) (PEG). Due to its high hydrophilicity PEG shows hardly any interactions with proteins and can be excreted through the kidneys up to molecular weights of approximately 30,000. Amphiphilic block copolymers, consisting of hydrophilic PEG blocks and hydrophobic blocks have been widely applied for the preparation of hydrogels
Figure (a). PLA and PLGA have been mostly used as the hydrophobic blocks. Other hydrophobic blocks include PCL and poly(D,L-3-methylglycolide) (PMG). These amphiphilic block copolymers self-assemble in water due to hydrophobic interactions and may form physically crosslinked hydrogels. PEG has also been derivatized withpolymerizable (meth)acrylate groups for the formation of hydrogels by photoirradiation or redox initiation. Another often used biocompatible polymer is poly(vinyl alcohol) (PVA). Similar to PEG, this polymer is protein repellant with the additional advantage that its many hydroxyl groups allow for easy chemical modification. PVA hydrogels have been mostly formed by photopolymerization of (degradable) PVA (meth)acrylate derivatives Figure (c). Poly(N-isopropylacrylamide) (PNIPAAm) (co)polymers have also been investigated as biomaterials.
Poly(organophosphazenes) present a new type of materials that degrade through hydrolysis. They may be prepared with a variety of side groups, thus offering a wide range of material properties.

Although hydrophilic polymers may be excreted by the kidneys dependent on their molecular weight, they become non-soluble when they are chemically crosslinked to form hydrogels. To allow for the degradation of hydrogels based on water-soluble, non-biodegradable polymers, such as PEG, PVA and PNIPAAm, biodegradable sequences, such as PLA or degradable peptide sequenceshave to be incorporated in the hydrogel network.

1.2.e.3.Hybrid hydrogels based on both synthetic and natural materials:

Cell-responsive hybrid hydrogels have been prepared by using a combination of PEG and additives such as chondroitin sulphate, collagen mimetic peptide and cell-adhesion and enzyme cleavable peptides. Temperature-responsive hybrid hydrogels have been prepared by combining natural polymers with PNIPAAm. Hybrid hydrogels that are pH-sensitive have been prepared by combining natural polymers with poly(acrylic acid). Natural polymers have also been combined with PLA to obtain degradable hydrogels and to tune the swelling properties.

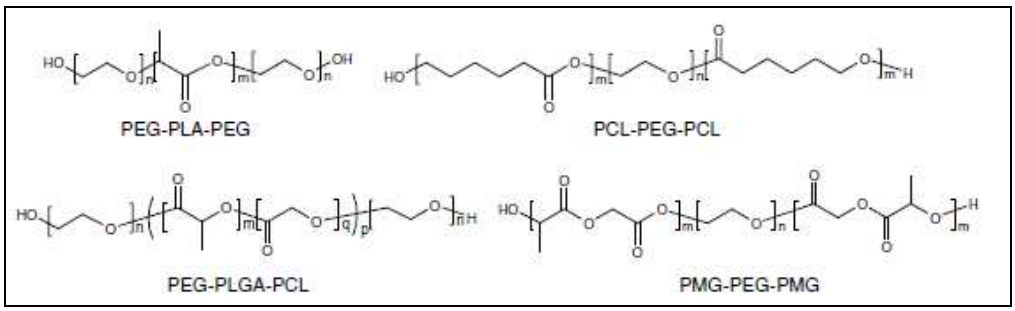
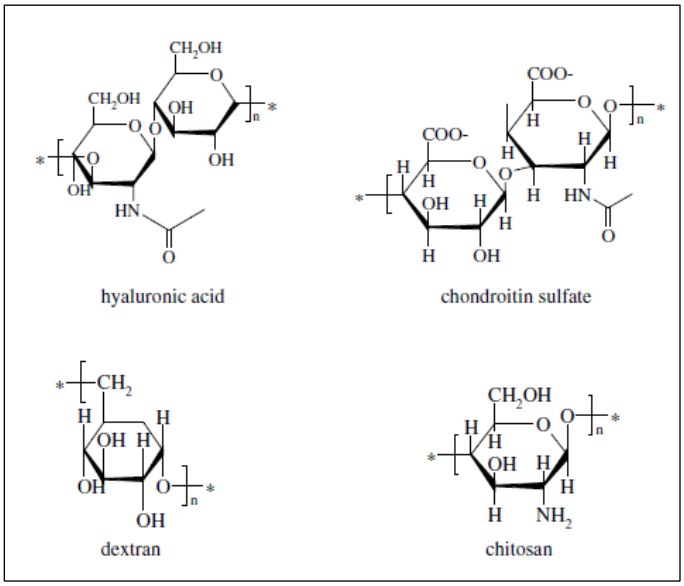


Figure (a). PEG- poly(hydroxy acid) block copolymers used for hydrogel preparation



Figure(b). Structural elements of polysaccharides used for hydrogel preparation

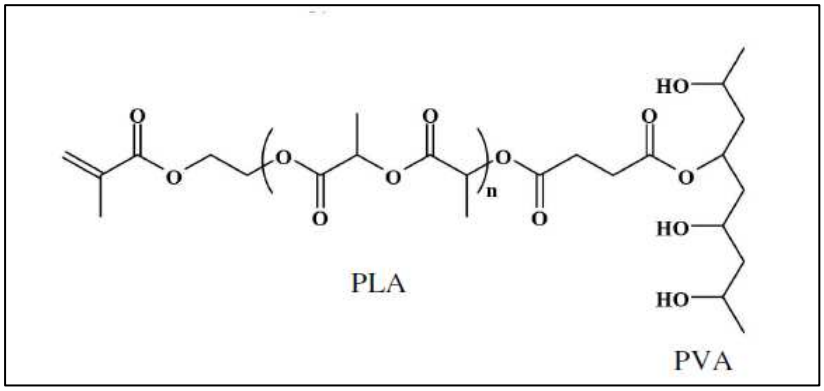


Figure (c). Degradable, photocrosslinkable PVA-PLA macromer.

1.3.Properties of Hydrogels:

1.3.1.Mechanical Properties:

For non biodegradable applications, it is essential that the carrier gel matrix maintain physical and mechanical integrity. Mechanical stability of the gel is, therefore, an important consideration when designing a therapeutic system. For example, drugs and other biomolecules must be protected from the harmful environments in the body such as, extreme pH environment before it is released at the required site. To this end, the carrier gel must be able to maintain its physical integrity and mechanical strength in order to prove an effective biomaterial. The strength of the material can be increased by incorporating crosslinking agents, co monomers, and increasing degree of crosslinking.

There is however an optimum degree of crosslinking, as a higher degree of crosslinking also leads to brittleness and less elasticity. Elasticity of the gel is important to give flexibility to the crosslinked chains, to facilitate movement of incorporated bioactive agent. Thus a compromise between mechanical strength and flexibility is necessary for appropriate use of these materials.

1.3.2.Biocompatible Properties:

It is important for synthetic materials, such as hydrogels, to be biocompatible and nontoxic in order for it to be a useful biomedical polymer. Most polymers used for biomedical application must pass a cytotoxicity and in-vivo toxicity tests.

Most toxicity problems associated with hydrogels arise due to unreacted monomers, oligomers and initiators that leach out during application. Thus an assessment of the potential toxicity of all materials used for fabrication of gel is an integral part of determining suitability of the gel for biological applications.

To lower chances of toxic effects, the use of initiators is being eliminated, with the advent of gamma irradiation as polymerization technique. Steps are also taken to eliminate contaminants from hydrogels, by repeated washing and treatment. Also kinetics of polymerization has been studied, so as to achieve higher conversion rates, and avoid unreacted monomers and side products.

1.3.3. Equilibrium properties of Hydrogels:

1.3.3.1Volume phase transition in Hydrogels:

When swelling equilibria of N-substituted acrylamide gels, such as N-isopropylacrylamide,N-n-propylacrylamide, Ncyclopropylacrylamide, N-ethoxyethylacrylamide gels [(40)], were measured in water at various temperature. It was observed that the gels showed thermoshrinking swelling behaviors and that the swelling behaviors were strongly dependent on the N-substitutes.

Swelling equilibria of the N-isopropylacrylamide gel were measured in the presence of additives (salts and organic compounds). The additives did not affect the swelling ratio but depressed the transition temperature.It is also observed that volume phase transitions also affected by external stimuli (pH, light ,temperature and electric field).

1.3.3.1.1.Effect of hydrotropes on volume phase transition :

In the volume phase transition (VPT) exhibited by poly(*N*-isopropylacrylamide) hydrogels the effect of hydrotropes on VPT was monitored[41]. Hydroxybenzenes, hydroxybenzoates, and benzenesulfonates, which constitute the class of hydrotropes, permit an assessment of subtle molecular and structural features on the VPT because ortho, meta, and para isomers differ in their hydrotropy.

Among the compounds studied, in a selected concentration range it was observed that dihydroxybenzoic acid was the most efficient in lowering the transition temperature and salicylate anion raises the transition temperature while *m*-hydroxybenzoate offers minimum perturbation. The results are indicative of entropic cooperativity of many interactions stabilizing a conformation as the driving force for the volume phase transition.

1.3.3.1.2.Effect of chemical structure on the volume-phase transition:

Neutral poly(*N*-isopropylacrylamide) (PIPAAm), poly(*N*,*N*-diethylacrylamide) (PDEAAm), and poly(*N*-isopropylmethacrylamide) (PIPMAm) hydrogels and their weakly charged counterparts[42] were studied using ultrasmall-angle x-ray scattering. The volume-phase transition in hydrogels was observed as an increase in the inhomogeneity correlation length of the networks. The change in inhomogeneity correlation length was abrupt in neutral PIPAAm and PIPMAm gels with increase in temperature but was continuous in neutral PDEAAm gels. Addition of ionic comonomer to the network backbone suppressed the volume-phase transition in poly(*N*-alkylacrylamide)s but not in PIPMAm.

The observed differences in temperature-induced volume change of these three polymers in water were explained by considering the hydrogen-bonding constraints on their thermal fluctuations. Both PIPAAm and PDEAAm undergo volume collapse since their thermal fluctuations are constrained by hydrogen bonding with water to an extent that beyond a critical temperature they seek entropic compensation. Although thermal fluctuations in both PIPAAm and PIPMAm are equally constrained, thermal energy of the latter can be relaxed via the rotation of α-methyl groups allowing it greater flexibility.

1.3.3.1.3.Effect of Hydrolysis and Temperature on the Volume-phase transitions:

The degree of hydrolysis of hydrogel also affects its VPT in a significant way. The unhydrolyzed hydrogels show only continuous VPT but with 60% hydrolysis in alkaline solution , volume change increases 500 folds [43,44]. Acetone concentration at which volume transition occurs increases with degree of hydrolysis VPT also occurs on temperature variation [45,46]. Hydrogels swells at higher temperature but collapses at lower temperature . Volume transition of N-i-PAAm

sodium acrylate copolymer gels in pure water is a function of temperature for copolymer compositions [47].

It has been observed that with increase in ionisable groups , volume changes at the transition increases and so does transition temperature .

1.3.3.1.4.Effect of *p*H and Ionic strength on the Volume-phase transitions:

Reversible phase transition of ionic gels responds to *p*H [48] and ion composition [49]. Discontinuous volume phase transitions in ionised acrylamide gels [43] . Presence of fixed charges on macromolecular chains determine large swelling of polymer due to equilibrium established between gel and external solution whose ionic strength strongly affects degree of swelling . On variation of pH or addition of salt to solvent , effective number of counter ions also varies as does the ionic osmotic pressure and hence swelling get affected .

1.3.4.Dynamic Properties of Hydrogels:

Polymeric network of a gel is constantly in random thermal motion giving rise to space and time fluctuation of polymer density . These density fluctuations reveal fundamental properties of gels and can be observed by light scattering[50-53] or neutron scattering techniques[54-56] .

Viscoelastic quantities have been investigated as a function of temperature and polymeric network [56,57].Temperature dependence of light scattering reveals critical behaviour of gels as temperature approaches critical points , intensity of scattered light increases to infinity and relaxation time slows down to zero [58].

1.3.5.Kinetic properties of hydrogels:

The most important property of hydrogel is its ability to imbibe water while elasticity of stretched network opposes osmotic swelling . Resultant of these two forces is swelling pressure and a pressure imposed on hydrogel that stops swelling equals the instantaneous swelling pressure .

If the osmotic pressure of a solution in contact with gel is increased by presence of solute , swelling pressure increases and swelling decreases . The swelling pressure **(P_{sw})** obeys the empirical relationship :

$$P_{sw} = K x C^{n} r$$

Here K and n are constants with values between 2and 3 and C is polymer network concentration [59]. Thus, swelling pressure exponentialy with polymer concentration .

1.4.Applications of Hydrogels:

1.4.1.Applications of Hydrogels in Drug Delivery:

Advances in recombinant protein technology have identified several protein and peptide therapeutics for disease treatment. However, the problem which plagued researchers was how to effectively deliver these biomolecules. Due to their large molecular weight, and three dimensional structure, the most commonly used route for drug administration is by intravenous or subcutaneous injection.

Unfortunately proteins and peptides are prone to proteolytic degradation, thus they experience short plasma circulation times and rapid renal clearance, leading to multiple daily injections or increased dosage in order to maintain the required drugtherapeutic levels . Multiple injections are difficult for the patient, while high doses might be toxic, and induce serious immune response. Hydrophobic polymeric controlled release formulations, such as PLGA, offer a sustained release mechanism in which drug release rates can manipulated by changing polymer molecular weight and composition.

These polymers however induce adverse effects to the encapsulated proteins or peptides during network preparation and delivery [60], as well as trigger the immune response. Hydrophilic hydrogels, on the other hand, provide relatively mild network fabrication technique and drug encapsulation conditions, making them the ideal material for use in drug delivery. Thus hydrogels are primarily used for encapsulation of bioactive materials and their subsequent controlled release. If designed properly, hydrogels can be used in a variety of applications such as sustained, targeted, or stealth biomolecule delivery. Hydrogel based delivery devices can be used for oral, ocular, epidermal and subcutaneous application. The Fig 1.1 below indicates various sites that are available for the application of hydrogels for drug delivery. These applications are discussed in detail below.

1.4.1.1.Drug Delivery in the GI Tract:

The ease of administration of drugs, and the large surface area for absorption makes the GI tract most popular route for drug delivery.

It is however, also a very complex route, so that versatile approaches are needed to deliver drugs for effective therapy. Hydrogel-based devices can be designed to deliver drugs locally to specific sites in the GI tract. For example, Patel and Amiji [61] proposed stomach –specific antibiotic drug delivery systems for the treatment of *Helicobacter pylori* infection in peptic ulcer disease. They developed cationic hydrogels with pH sensitive swelling and drug release properties for antibiotic delivery in the acidic environment of the stomach. There are still many drawbacks for peroral delivery of peptides and proteins to GI tract, like protein inactivation by digestive enzymes in the GI tract and poor epithelial permeability of the drugs.

However certain hydrogels may overcome some of these problems by appropriate molecular design or formulation. For example Akiyama [62] reported novel peroral dosage forms of hydrogel formulations with protease inhibitory activities. Recently oral insulin delivery using pH responsive complexation hydrogels was reported [63] .

The hydrogels used were crosslinked copolymers of PMMA with graft chains of polyethylene glycol

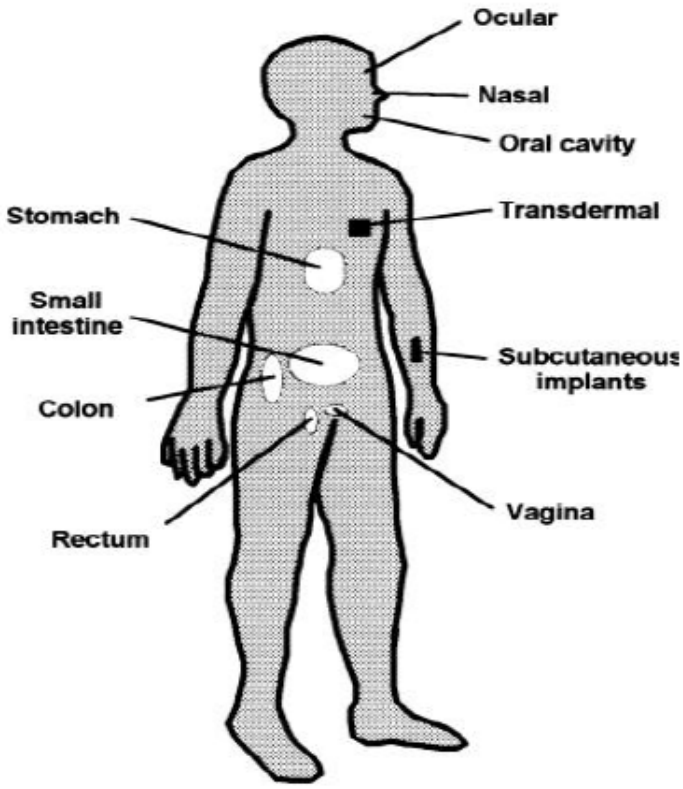


Figure 1.1 Tissue locations[60]. applicable for hydrogel based drug delivery systems .

These hydrogels protect the insulin in the harsh, acidic environment of the stomach before releasing the drug in the small intestine.

The colonic region has also been considered as a possible absorption site for orally administered proteins and peptides, mostly due to a lower proteolytic activity in comparison to that in the small intestine. Several hydrogels are currently being investigated as potential devices for colon-specific drug delivery. These include chemically or physically crosslinked polysaccharides such as dextran [64], guar gum [65] and insulin [66]. They are designed to be highly swollen or degraded in the presence of colonic enzymes or microflora, providing colon-specificity in drug delivery.

1.4.1.2.Rectal Delivery:

This route has been used to deliver many types of drugs for treatment of diseases associated with the rectum, such as hemorrhoids. This route is an ideal way to administer drugs suffering heavy first-pass metabolism. There are however, some drawbacks associated with rectal delivery.

For example, due to discomfort arising from given dosage forms, there is substantial variability in patient‟s acceptance of treatment Also, if drugs diffusing out of the suppositories are delivered in an uncontrolled manner, they are unable to be retained at a specific position in the rectum, and tend

to migrate upwards to the colon. This leads to variation of availability of drugs, especially those that undergo extensive first-pass elimination.

Hydrogels offer a way in which to overcome these limitations, provided that the hydrogels show bioadhesive properties. It was reported [67] that increased bioavailability of propanol subject to extensive first-pass metabolism was observed by adding certain mucoadhesive polymeric compounds to poloxamer –based thermally gelling suppositories. The polymeric compounds tested were polycarbophil and sodium alginate. Miyazaki et al. [68] investigated the potential application of xyloglucan gels with a thermal gelling property as matrices for drug delivery. Another important issue in rectal drug delivery is to avoid rectal irritation. The products discussed above, indicated no such mucosal irritation after drug administration.

1.4.1.3.Ocular Delivery:

Drug delivery to the eye is difficult due to its protective mechanisms, such as effective tear drainage, blinking, and low permeability of the cornea . Thus, eye drops containing drug solution tends to be eliminated rapidly from the eye and the drugs show limited absorption, leading to poor ophthalmic bioavailability. Due to the short retention time, a frequent dosing regimen is necessary for required therapeutic efficacy. These challenges have motivated researchers to develop drug delivery systems that provide prolonged residence time.

The earlier dosage forms, such as suspension and ointments could be retained in the eye, but sometimes gave patients an unpleasant feeling because of the nature of solids and semisolids. Hydrogels, because of their elastic properties can represent an ocular drainage-resistant device. In-situ forming hydrogels are attractive as an ocular drug delivery system because of their facility in dosing as a liquid, and long term retention property as a gel after dosing.

Cohen et al [62] developed an in-situ gelling system of alginate with high gluronic acid contents for the ophthalmic delivery of pilocarpine. This system extended the duration of the pilocarpine to 10 hr, compared to 3 hr when pilocarpine nitrate was dosed as a solution. Chetoni et al[68] reported silicone rubber hydrogel composite ophthalmic inserts.

An in-vivo study using rabbits showed a prolonged release of oxytetracycline from the inserts for several days.

1.4.1.4.Transdermal Delivery:

Drug delivery to the skin has been generally used to treat skin diseases or for disinfection of the skin. In recent years, however a transdermal route for the delivery of drugs has been investigated. Swollen hydrogels can be delivered for long duration and can be easily removed. These hydrogels can also bypass hepatic first-class metabolism, and are more comfortable for the patient.

Hydrogel based delivery devices have been proposed by Sun et al. [69] , such as composite membranes of crosslinked PHEMA with a woven polyester support.

Also hydrogels have been reported[70] which have been obtained by the copolymerization of bovine serum albumin (BSA) and PEG. These hydrogels can be used as controlled release
devices in the field of wound dressing. Hubbell[71] has also carried out extensive research on in-situ photopolymerization made from terminally diacrylated ABA block copolymers of lactic acid oligomers (A) and PEG (B) for barriers and local drug delivery in the control of wound healing. Current research in this field is now focused on electrically-assisted delivery using iontophoresis and electroporation[61]. Hydrogel-based formulations are being looked at for transdermal iontophoresis to obtain enhanced permeation of products in question such as, hormones[68] and nicotine.

1.4.1.5.Subcutaneous Delivery:

Among the varied possible pharmaceutical applications of hydrogels, the most substantial application is probably in implantable therapeutics. Implantable devices that are subcutaneously inserted tend to illicit immune response of the body, leading to inflammation, carcinogenicity and immunogenicity. Thus biocompatibility becomes a major issue, and all implantable materials must be compatible with the body. Hydrogels are an ideal candidate for implantable materials.
They have high water content, environment similar to biological tissue, making them relatively biocompatible. They also have other properties which make them a viable choice [72] ; (1) minimal mechanical irritation upon in-vivo implantation due to their
soft, elastic properties (2) prevention of protein absorption and cell adhesion arising from the low interfacial tension between water and hydrogels (3) broad acceptability for individual drugs with different hydrophilicities and molecular sizes, and (4) can manipulate crosslinking density and swelling for release of incorporated drug in specific manner. Thus hydrogels are an ideal material to be used for delivery of proteins and peptides. Hydrogel formulations for subcutaneous delivery of anticancer drugs have been proposed.
For example, crosslinked PHEMA was applied to cyratabine (Ara-C) .
Current studies on implantable hydrogels are leading towards the development of biodegradable systems, which don‟t require surgical removal once the drug has been administered. Biodegradable PEG hydrogels are now at the forefront of this research, and several novel systems have been developed. One type is synthesized via a polycondensation reaction between functional PEG acids and branched PEG polyols. Another type is PEG based hydrogels having functional groups in which the protein drugs can be covalently attached to the gel network via
ester linkages. In this case, the release of the immobilized proteins would be controlled by the hydrolysis of ester linkage between the gel and protein, followed by diffusion of protein, and degradation of gel.

1.4.2.Applications of Hydrogels in Tissue engineering:

A **fibrin scaffold** is a network of protein that holds together and supports a variety of living tissues. It is produced naturally by the body after injury, but also can be engineered as a tissue substitute to speed healing. The scaffold consists of naturally occurring biomaterials composed of a cross-linked fibrin network and has a broad use

in biomedical applications. Fibrin consists of the blood proteins fibrinogen and thrombin which participate in blood clotting. Fibrin glue or fibrin sealant is also referred to as a fibrin based scaffold and used to control surgical bleeding, speed wound healing, seal off hollow body organs or cover holes made by standard sutures, and provide slow-release delivery of medications like antibiotics to tissues exposed.[73,74]

Fibrin scaffold use is helpful in repairing injuries to the urinary tract,[75] liver[76] lung,[77] spleen,[78] kidney,[79] and heart.[80] In biomedical research, fibrin scaffolds have been used to fill bone cavities, repair neurons, heart valves,[81] vascular grafts[82] and the surface of the eye.

1.4.3.Application of Hydrogel in Agriculture[83]:

There are two main types of agricultural hydrogels, each with its own purpose. Both are polyacrylamide (PAM) polymers, but the linear PAM is used primarily for the prevention of soil erosion[83], while the cross-linked PAM is used to absorb large quantities of water and then release it over time (known as Reclaiming and Ameliorating Polymer Gel) . The latter can be found in garden stores under the name of "super-absorbent crystals" or something similar. The effectiveness of linear PAM has been proven many times over the last several years, while the use of cross-linked PAM is under some debate, as certain soil and environmental conditions can force variable results.

Hydrogels has also been used for fixation of herbicides ,for controlled release of insecticides and fertilizers .

1.4.4.Applications of Hydrogels in Biosensor:

Hydrogels are valuable materials for use in biosensors [84] . They can be used for immobilization as well as for creating protecting layers controlling diffusion and enhancing biocompatibility. Highly stable biosensors use hydrogels for entrapment of enzymes on microelectrodes.

Fluorescent glucose biosensors are devices that measure the concentration of glucose in diabetic patients by means of sensitive protein that relays the concentration by means of fluorescence, an alternative to amperometric sension of glucose.

The majority of these sensors, rely on entrapping the protein in hydrogels, as these are more sturdy and protect the protein more than a simple coating or membrane.

Several types of hydrogel exist that have been used to entrap small molecules such as dyes,[85] biomolecules, such as enzymes[86] or whole cells.[87,88] In the case of protein, they can work either by physically entrapping the protein having pores smaller than the proteins or by chemical linkage of the protein to the matrix. In physically entrapping gels, the protein has to be added when the gel is crosslinked, so the conditions used must not damage the protein, excluding the hydrogel.

Microarrays based on poly(ethylene glycol)(PEG) hydrogel is responsive to phenol and carry out enzyme-catalyzed oxidation of phenol to produce quinones , thus used in biosensor based on phenol[89].

A poly(vinyl alcohol) (PVA) cross-linked with poly(acrylic acid) (PAA) swells with

pH as a result of an osmotic effect. Reversible swelling of a PVA/PAA hydrogel sensitive to pH, resulting in refractive index changes in the hydrogel layer, providing information on the stage of the wound healing process[90].

A biotin-coated quartz crystal microbalance (QCM) chip was prepared by dip-coating a long-chain alkanethiol-modified crystal with precoupled dextran-biotin hydrogels. The resulting biotin chip was used to affinity-immobilize streptavidin (SAv) and was then further employed for various biosensor assays (e.g., in immunoassay and peptide-displaying cell detection). [91].

Poly (ethylene glycol) (PEG) hydrogel photopatterning was employed to Enzyme-based electrodes ,(an important class of biosensors) where byproducts of enzymatic breakdown of an analyte are detected electrochemically[92].

1.4.5.Hydrogel in environmental study:

Hydrogels, based on 2-acrylamido-2-methyl-1-propansulfonic acid (AMPS) [93] were synthesized via photopolymerization technique and used for the preparation of magnetic responsive composite hydrogels. These composite hydrogels with magnetic properties were further utilized for the removal of toxic metal ions such as Cd(II), Co(II), Fe(II), Pb(II), Ni(II), Cu(II) and Cr(III) from aqueous environments. The magnetic nanoparticles (MNPs) were prepared in situ process in poly(acrylamide)-gum acacia (PAM-GA) hydrogels[94] . These hydrogel magnetic nanocomposites were utilized for the removal of toxic metal ions such as Co (II), Ni (II), Cu (II) and protein purification. (PAM-GA) hydrogels were synthesized by employing free radical polymerization using *N*,*N*-methylenebisacrylamide (MBA) as cross-linker andammonium persulfate/*N*,*N*,*N1*,*N1*-tetramethylethylenediamine (APS/TMEDA) as redoxinitiating pair.

Uranyl ion adsorption from aqueous solutions has been investigated by chemically crosslinked acrylamide/sodium acrylate (CASA) hydrogels[95].

Application of poly (3-Acrylamidopropyl)-trimethylammonium chloride (PAPTMACl) hydrogels[96] were synthesized in the form of small cylinders, with using N, N'-methylene-bisacrylamide (MBA) as crosslinker. N,N,N',N'-tetramethylethylenediamine (TEMED) was used as an accelerator, and ammonium persulfate (APS) was used as redox initiator. as adsorbents for removal of toxic anions such as arsenate from water were investigated.

Anionic poly(sodium acrylate), PANa[97] , hydrogels bearing negatively charged $-COO^-$ groups were used as sorbents for the removal of colored organic or inorganic model pollutants, namely Crystal Violet and Cu(II), from water. It was found that PANa hydrogels adsorb stronger Cu(II) ions than Crystal Violet, as a consequence of the formation of coordination complexes between the hydrogel and the metal ions, while just electrostatic interactions are the major driving forces for Crystal Violet.

Removal of Pb(II) and Cd(II) ions from aqueous solutions using guanidine modified hydrogels[98]

1.5.Aims and Objctives of This Project

1.To use Natural resources to get Hydrogel.

2.To copolymerise reactive substances present in fruits with Acryl Amide using KPS as initiator .

3.To synthesise hydrogel networks of copolymers by crosslinking reactions in presence of N,N-MBAAm as crosslinking material .

4.To study some structural aspects of hydrogels by characterisation using techniques like FTIR , SEM and X-RD .

5. To study swelling of hydrogel in water as function of time, temperature and pH of medium .

6.To study some speciality application of hydrogel like superabsorbency , hazardous metal ion uptake properties at various parameters like time ,pH, and temperature; for investigation of potential application of the hydrogels in environment management.

CHAPTER 2
SYNTHESIS OF HYDROGEL

2.1.Preparation Methods of Hydrogels

Hydrogels are polymeric networks. This implies that crosslinks have to be present in order to avoid dissolution of the hydrophilic polymer chain in aqueous solution.Hydrogels are most frequently used for controlled release of bioactive agents and for encapsulation of cells and biomolecules. In many of these cases the three dimensional structure of the hydrogels have to disintegrate into harmless non toxic products to ensure biocompatibility of the gel. The nature of the degradation products can be tailored by a proper selection of the hydrogel building blocks. Keeping this consideration in mind, various chemical and physical crosslinking methods are used today for the design of biocompatible hydrogels. Chemically crosslinked gels have ionic or covalent bonds between polymer chains. Even though this leads to more mechanical stability, some of the crosslinking agents used can be toxic, and give unwanted reactions, thus rendering the hydrogel unsuitable for biological use. These adverse effects can be removed with the use of physically crosslinked gels. In physically crosslinked gels, dissolution is prevented by physical interactions between different polymer chains. Both of these methods are used today for preparation of synthetic hydrogels and are discussed in detail. In this paper, the hydrogels were crossslinked via free radical polymerization on exposure to UV radiation, without the use of a crosslinking agent.

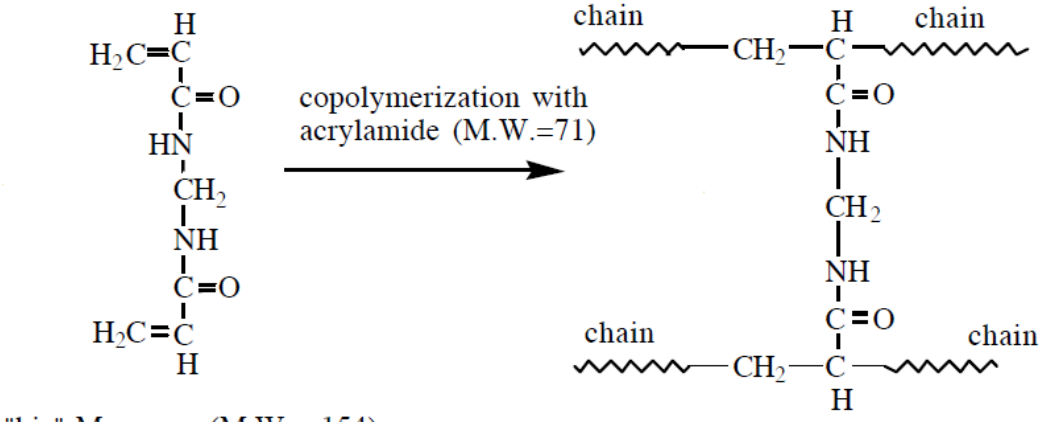
2.1.1. Chemically Crosslinked Gels

As stated earlier, chemically crosslinked gels are mechanically quite stable due to the ionic and covalent bond which comprises these gels. However the addition of crosslinking agent leads to adverse effects if the compound is toxic, which on liberation in the body becomes quite harmful. The various methods for chemical crosslinking are as follows:

Crosslinking of Polymers

In this method chemically crosslinked gels are formed by radical polymerization of low molecular weight monomers, or branched homopolymers, or copolymers in the presence of crosslinking agent. This reaction is mostly carried out in solution for biomedical applications. Most hydrophilic polymers have pendant hydroxyl group, thus agents such as aldehydes, maleic and oxalic acid, dimethylurea, diisocyanates etc that condense when organic hydroxyl groups are used as crosslinking agents.

The solvent used for these reactions is usually water, but methanol, ethanol and benzyl alcohol have also been used. These solvents can be used only if after formation of network structure, the solvent can be exchanged with water.



"bis" Monomer (M.W.= 154)

End-linking and crosslinking reactions may also occur in the absence of cross-linking agents if a free radical initiator can be used which forms free radicals in the backbone chain.

2.1.1.1 Copolymerization/Crosslinking Reactions

Copolymerization reactions are used to produce polymer gels, Many hydrogels are produced in this fashion, for example poly (hydroxyalkyl methylacrylates). Initiators used in these reactions are radical and anionic initiators. Various initiators are used, such as Azobisisobutyronitrile (AIBN), benzoyl peroxide etc. Solvents can be added during the reaction to decrease the viscosity of the solution.

2.1.1.2.Crosslinking by High Energy Radiation

High energy radiation, such as gamma[(1)]and electron beam radiation can be used to polymerize unsaturated compounds. Water soluble polymers derivatized with vinyl groups can be converted into hydrogels using high energy radiation. For example, PEG derivatized to PEGDA can form hydrogels once irradiated with UV radiations. Polymers without additional vinyl groups can also be crosslinked via radiation. On exposure to gamma or electron beam radiation, aqueous solutions of polymers form radicals on the polymer chains (e.g by the hemolytic scission of C-H bonds). Also the radiolysis of water molecules generates the formation of hydroxyl groups which can attack polymer chains also resulting in the formation of microradicals. Recombination of these microradicals on different chains results in the formation of covalent bonds and finally in a crosslinked structure. The swelling and permeability characteristics of the gel depend on the extent of polymerization, a function of polymer and radiation dose (in general crosslinking density increases with increasing radiation dose). The
advantage of using this process for gel formation is that in can be done in water under mild conditions without the use of a crosslinking agent. However there are some drawbacks to using this method, the bioactive material has to be loaded after gel formation, as irradiation might damage the agent. Also in some gels like PEG and PVA, the crosslinks consist of C-C bonds, which are not biodegradable.

Crosslinking Using Enzymes

Recently a new method was published[(2)]using an enzyme to synthesize PEG-based hydrogels. A tetrahydroxy PEG was functionalized with addition of glutaminyl groups and networks were formed by addition of transglutaminase into solution of

PEG and poly (lysine-cophenylalanine). This enzyme catalyzed reaction between γ-carboxamide group of PEG and the ε- amine group of lysine to obtain an amide linkage between polymers. The gel properties can be tailored by changing ratios of PEG and lysine.

2.1.2. Physically Crosslinked Gels

Chemically crosslinked gels imply use of a crosslinking agent, which is often toxic. This requires that the crosslinking agent be removed from gel, which can affect the gel integrity. For these reasons, physically crosslinked gels are now coming into prominence. Several methods have been investigated exploring preparation of physically crosslinked gels. Below are mentioned some of the most widely used methods and their areas of application.

2.1.2.1. Crosslinking by Ionic Interactions

An example of crosslinking via ionic interactions is crosslinking of Alginate. Alginate consists of glucuronic acid residues and mannuronic residues and can be crosslinked by calcium ions. Crosslinking can be carried out at normal temperature and pH. These gels are used as matrix for encapsulation of cells and for release of proteins. Also Chitosan based hydrogels, as well as dextran based hydrogels, crosslinked with potassium ions are also other gels synthesized with ionic interactions. In addition to anionic polymers being crosslinked with metallic ions, hydrogels can also be obtained by complexation of polyanions and polycations.

2.1.2.2. Crosslinking by Crystallization

An aqueous solution of PVA that undergoes a freeze-thaw process yields a strong highly elastic gel. Gel formation is attributed to the formation of PVA crystallites which act as physical crosslinking sites in the network. The gel properties could be modified by varying polymer concentration, temperature, and freezing and thawing cycle times. These gels have been shown to be useful for drug release [(3)].

2.1.2.3. Crosslinking by Hydrogen Bonds

Poly(acrylic acid) and poly(methacrylic acid) form complexes with poly(ethylene glycol) by hydrogen bonding between the oxygen of the poly(ethylene glycol) and the carboxylic acid group of poly((meth)acrylic acid) [(4)]. Also hydrogen bonding has been observed in poly (methacrylic acid-g-ethylene glycol). The hydrogen bonds are only formed when the carboxylic acid groups are protonated. This also implies that the swelling of gels is pH dependent. Recently a hydrogel system was developed using the principle of DNA hybridization via hydrogen bonding [(5)]. In this approach, oligodeoxyribonucleotides were coupled to a water soluble polymer. Hydrogels were prepared by addition of a complementary oligodinucleotide (ODN) either conjugated to the same water soluble polymer or, in its free form, to an aqueous solution of the ODN derivatized water soluble copolymer.

2.1.2.4.By Protein Interaction

Genetic Engineering has also been used for the preparation of hydrogels. The major advantage is that the sequence of peptides and, therefore its physical and chemical properties can be precisely controlled by the proper design of the genetic code in synthetic DNA sequences [(6)]. Cappello and colleagues prepared sequential block copolymers containing a repetition of silk-like and elastine –like blocks, in

which the insoluble silk like segments are associated in the form of aligned hydrogen bonded beta strands or sheets. These hydrogels can also be used for drug delivery with drug release influenced by concentration, polymer composition, and temperature. Crosslinking by antigen-antibody interaction was also performed [7], in which an antigen (rabbit IgG) was grafted to chemically crosslinked polyarylaide in the presence of an additional crosslinker. Additionally hydrogels have been prepared by immobilizing both the antigen and the antibody in the form of an interpenetrate network polymer network. This approach might permit drug delivery in response to specific antigen.

This chapter will deal with the synthesis of hydrogel based on acrylamide.

All hydrogels prepared in my project are Acrylamide based.

In this chapter co monomers Acrylic acid, Meth acrylic acid, Cane juice(sugar is main constituent), Sapodilla(Scientific name: *Manilkara zapota)* extract (sugar is main constituent), Pineapple(Scientific name: *Ananas comosus*) juice(sugar is main constituent) were used.

Six hydrogels were synthesised in this chapter.

Initiator used was *Potassium Peroxydisulphate* (**KPS- $K_2S_2O_8$**).

Cross linker used was N,N'-*Methylenebisacrylamide* (**N,N-MBAAm**).

List hydrogels prepared.

1.**Hydrogel 1 :** Polyacrylamide

2.**Hydrogel 2 :** Poly(Acrylamide-co-Acrylic acid)

3.**Hydrogel 3 :** Poly(Acrylamide-co-Meth acrylic acid)

4.**Hydrogel 4 :** Poly(Acrylamide-co-Sucrose from cane juice)

5.**Hydrogel 5 :** Poly(Acrylamide-co-Sapodilla extract)

6.**Hydrogel 6 :** Poly(Acrylamide-co-Pineapple juice)

Note: Tables are given for composition of juices and extract.

2.2.1.HYDROGEL 1

It is based on homo polymer of Acrylamide.

Monomer:

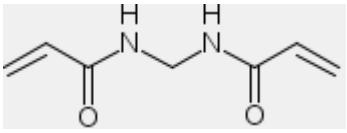
Acrylamide (99%) => (C_3H_5NO): CH_2=CHCONH$_2$
From SRL

Initiator:

KPS (98%) => **$K_2S_2O_8$**
From S.D.Finechem .Ltd

Crosslinker:

N,N′-*Methylenebisacrylamide* (**N,N-MBAAm**)(98%) . **$C_7H_{10}N_2O_2$**



From Merck.

Media: DMW(H_2O)

Apparatus:

Test tube, Water bath, Magnetic stirrer, Stand, Electrical balance Thermometer etc.

Procedure:

Take 5 gram Acrylamide; dissolved it in water and make volume up to 3/4th of test tube .Shake and make solution homogeneous. Now add .01% amount of initiator and make homogeneous solution. Finally add .02% amount of crosslinker and shake well. Now put the test tube on water bath .Maintain the temperature at 60 to70^{0}C. It will take nearly 40 min to form a tight transparent gelly mass .This is so called Polyacrylamide hydrogel named as HYDROGEL 1 in my project. Now break the test tube gently and wash hydrogel with DMW to remove un polymerised monomer and other unreacted chemicals. Now cut test tube shaped hydrogel in small pellet shape. Put all pellets in petry dish and put it in oven at 60^{0}C. Heat it till the gross weight is smaller than the chemicals taken.

Precaution:

Acrylamide is a carcinogenic and neurotoxic material so handle it properly.
Avoid over heating otherwise polymer will may degrade.
Initiator and crosslinking materials are taken as minimum as possible.
Solution must be homogeneous for preparation of hydrogel and should be made in order as prescribed in procedure.

2.2.2.HYDROGEL 2

It is based on copolymer of Acrylamide and Acrylic acid

Monomer:

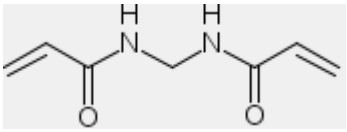
Acrylamide (99%) => (C_3H_5NO): **CH_2=CHCONH$_2$**
From **SRL**
Acrylic acid (99%) => ($C_3H_4O_2$): **CH_2=CHCOOH**
From **CDH**

Initiator:

KPS (98%) => **$K_2S_2O_8$**
From S.D.Finechem .Ltd

Crosslinker:

N,N′-*Methylenebisacrylamide* (**N,N-MBAAm**)(98%) . **$C_7H_{10}N_2O_2$**



From Merck.

Media:

DMW (H_2O)

Apparatus:

Test tube, Water bath, Magnetic stirrer, Stand, Electrical balance Thermometer etc.

Procedure:

Take 5 gram Acrylamide; dissolved it in water; now add equimolar amount of Acrylic acid and make volume up to 3/4th of test tube .Shake and make solution homogeneous. Now add .01% amount of initiator and make homogeneous solution. Finally add .02% amount of crosslinker and shake well. Now put the test tube on water bath .Maintain the temperature at 60 to70^{0}C. It will take nearly 55 min to form a tight nearly transparent gelly mass .This is so called Poly(acrylamide-co-acrylic acid)hydrogel named as HYDROGEL 2 in my project. Now break the test tube gently and wash hydrogel with DMW to remove unpolymerised monomer and other unreacted chemicals. Now cut test tube shaped hydrogel in small pellet shape. Put all pellets in petry dish and put it in oven at 60^{0}C. Heat it till the gross weight is smaller than the chemicals taken.

Precaution:

Acrylamide is a carcinogenic and neurotoxic material so handle it properly.

Avoid over heating otherwise polymer will may degrade.

Initiator and crosslinking materials are taken as minimum as possible.

Solution must be homogeneous for preparation of hydrogel and should be made in order as prescribed in procedure.

Both monomers must be in equimolar amount.

2.2.3.HYDROGEL 3

It is based on copolymer of Acrylamide and Methacrylic acid

Monomer:

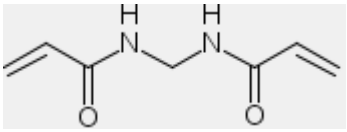
Acrylamide (99%) => (C_3H_5NO): **CH_2=CHCONH$_2$**
From **SRL**
Methacrylic acid (99%) => ($C_4H_6O_2$): **CH_2=C(Me)COOH**
From **SRL**

Initiator:

KPS (98%) => **$K_2S_2O_8$**
From S.D.Finechem .Ltd

Crosslinker:

N,N′-*Methylenebisacrylamide* (**N,N-MBAAm**)(98%) . **$C_7H_{10}N_2O_2$**



From Merck.

Media:

DMW (H_2O)

Apparatus:

Test tube, Water bath, Magnetic stirrer, Stand, Electrical balance Thermometer etc.

Procedure:

Take 5 gram Acrylamide; dissolved it in water; now add equimolar amount of Methacrylic acid and make volume up to 3/4th of test tube .Shake and make solution homogeneous. Now add .01% amount of initiator and make homogeneous solution. Finally add .02% amount of crosslinker and shake well. Now put the test tube on water bath .Maintain the temperature at 60 to70^{0}C. It will take nearly 50 min to form a tight nearly transparent gelly mass .This is so called Poly(acrylamide-co-Methacrylic acid)hydrogel named as HYDROGEL 3 in my project. Now break the test tube gently and wash hydrogel with DMW to remove unpolymerised monomer and other unreacted chemicals. Now cut test tube shaped hydrogel in small pellet shape. Put all pellets in petry dish and put it in oven at 60^{0}C. Heat it till the gross weight is smaller than the chemicals taken.

Precaution:

Acrylamide is a carcinogenic and neurotoxic material so handle it properly.

Avoid over heating otherwise polymer will may degrade.

Initiator and crosslinking materials are taken as minimum as possible.

Solution must be homogeneous for preparation of hydrogel and should be made in order as prescribed in procedure.

Both monomers must be in equimolar amount.

Handle Methacrylic acid gently because it has pungent smell which may cause headache.

2.2.4.HYDROGEL 4

It is based on copolymer of Acrylamide and Sugar from cane juice.

Monomer:

Acrylamide (99%) => (C_3H_5NO): **CH_2=CHCONH$_2$**

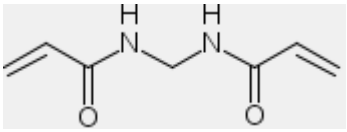
From **SRL**

Freshly prepared cane juice. For sugar ($C_{12}H_{22}O_{11}$) and other monosaccharides.

Initiator: KPS (98%) => **$K_2S_2O_8$**

From S.D.Finechem .Ltd

Crosslinker: N,N′-*Methylenebisacrylamide* (**N,N-MBAAm**)(98%) . **$C_7H_{10}N_2O_2$**



From Merck.

Media: DMW (H_2O)

Apparatus: Test tube, Water bath, Magnetic stirrer, Stand, Electrical balance Thermometer etc.

Procedure:

Take 5 gram Acrylamide; dissolved it directly in filtered juice and make volume 3/4th of test tube with juice .Shake and make solution homogeneous. Now add .01% amount of initiator and make homogeneous solution. Finally add .02% amount of crosslinker and shake well. Now put the test tube on water bath .Maintain the temperature at 60 to70^{0}C. It will take nearly 1hour to form a tight yellowish transparent gelly mass .This is so called Poly(acrylamide- co -sugar)hydrogel named as HYDROGEL 4 in my project. Now break the test tube gently and wash hydrogel with DMW to remove unpolymerised monomer and other unreacted chemicals. Now cut test tube shaped hydrogel in small pellet shape. Put all pellets in petry dish and put it in oven at 60^{0}C. Heat it till the gross weight is smaller than the chemicals taken.

Precaution:

Acrylamide is a carcinogenic and neurotoxic material so handle it properly.

Avoid over heating otherwise polymer will may degrade.

Initiator and crosslinking materials are taken as minimum as possible.

Solution must be homogeneous for preparation of hydrogel and should be made in order as prescribed in procedure.

Juice must be freshly prepared and filtered multi times to get clear sugar solution.

2.2.5.HYDROGEL 5

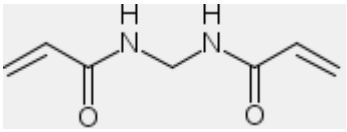
It is based on copolymer of Acrylamide and Sugar from sapodilla extract.

Monomer:

Acrylamide (99%) => (C_3H_5NO): **CH_2=CHCONH$_2$**
From **SRL**
Freshly prepared sapodilla extract for carbohydrates.

Initiator: KPS (98%) => **$K_2S_2O_8$**
From S.D.Finechem .Ltd

Crosslinker: N,N′-*Methylenebisacrylamide* (**N,N-MBAAm**)(98%) . **$C_7H_{10}N_2O_2$**



From Merck.

Media: DMW (H_2O)

Apparatus: Test tube, Water bath, Magnetic stirrer, Stand, Electrical balance Thermometer etc.

Procedure:

Take 5 gram Acrylamide; dissolved it directly in freshly prepared & filtered sapodilla extract and make volume 3/4th of test tube with extract .Shake and make solution homogeneous. Now add .01% amount of initiator and make homogeneous solution. Finally add .02% amount of crosslinker and shake well. Now put the test tube on water bath .Maintain the temperature at 60 to70^{0}C. It will take nearly 1hour to form a tight nearly transparent gelly mass .This is so called Poly(acrylamide- co – sapodilla extract)hydrogel named as HYDROGEL 5 in my project. Now break the test tube gently and wash hydrogel with DMW to remove unpolymerised monomer and other unreacted chemicals. Now cut test tube shaped hydrogel in small pellet shape. Put all pellets in petry dish and put it in oven at 60^{0}C. Heat it till the gross weight is smaller than the chemicals taken.

Precaution:

Acrylamide is a carcinogenic and neurotoxic material so handle it properly.

Avoid over heating otherwise polymer will may degrade.

Initiator and crosslinking materials are taken as minimum as possible.

Solution must be homogeneous for preparation of hydrogel and should be made in order as prescribed in procedure.

Extract must be freshly prepared and filtered multi times to get clear sugar solution.

2.2.6.HYDROGEL 6

It is based on copolymer of Acrylamide and Sugar from Pineapple juice.

Monomer:

Acrylamide (99%) => (C_3H_5NO): **CH_2=CHCONH$_2$**

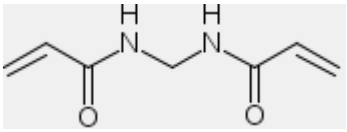
From **SRL**

Freshly prepared Pineapple juice for sugars .

Initiator: KPS (98%) => **$K_2S_2O_8$**

From S.D.Finechem .Ltd

Crosslinker: N,N′-*Methylenebisacrylamide* (**N,N-MBAAm**)(98%) . **$C_7H_{10}N_2O_2$**



From Merck.

Media: DMW (H_2O)

Apparatus: Test tube, Water bath, Magnetic stirrer, Stand, Electrical balance Thermometer etc.

Procedure:

Take 5 gram Acrylamide; dissolved it directly in freshly prepared & filtered Pineapple juice and make volume 3/4th of test tube with juice .Shake and make solution homogeneous. Now add .01% amount of initiator and make homogeneous solution. Finally add .02% amount of crosslinker and shake well. Now put the test tube on water bath .Maintain the temperature at 60 to70^{0}C. It will take nearly 1hour to form a tight nearly transparent gelly mass .This is so called Poly(acrylamide- co –Pineapple juice)hydrogel named as HYDROGEL 6 in my project. Now break the test tube gently and wash hydrogel with DMW to remove unpolymerised monomer and other unreacted chemicals. Now cut test tube shaped hydrogel in small pellet shape. Put all pellets in petry dish and put it in oven at 60^{0}C. Heat it till the gross weight is smaller than the chemicals taken.

Precaution:

Acrylamide is a carcinogenic and neurotoxic material so handle it properly.

Avoid over heating otherwise polymer will may degrade.

Initiator and crosslinking materials are taken as minimum as possible.

Solution must be homogeneous for preparation of hydrogel and should be made in order as prescribed in procedure.

Juice must be freshly prepared and filtered multi times to get clear sugar solution.

Table 1: For composition of cane juice[8]

Juice composition

		% Bx
Sugars	Sucrose	81-87
	Reducing sugars	3-6
	Oligosaccharides	0,06-0,6
	Polysaccharides[a,b] (including gums and dextrans)	0,2-0,8
Salts	Inorganic salts	1,5-3,7
Organic non-sugars	Organic acids	0,7-1,3
	Amino acids	0,5-2,5
	Dextrans[a]	0,1-0,6
	Starch[b,c]	0,11-0,5
	Gums	0,02-0,05
	Waxes, fats, phospholipids	0,05-0,15
	Colourants	0,1
Insolubles	Sand, bagasse, etc	0,15-1

a Ravelo *et al.* (1991a, b)
b Bruijn (1966)
c Alexander (1954)

Above % amount of different materials is regarding total solid in cane juice

COMPOSITION OF SUGARCANE JUICE [9]

PARAMETER [VALUE (%)] Water 70 to 75% Sucrose 11 to 16% (avg. = 13.0%) Reducing sugars 0.4 to 2% Organic non-sugars 0.5 to 1% Mineral matters 0.5 to 1% Fiber 10 to 16%

Sugarcane contains about 70% of water, in which sucrose & other substances are held in solution, forming about 88% by weight of juice in the stem. The remaining 12% represents the insoluble cane fiber component. The cane juice has an acidic pH ranging between 4.9 to 5.5.

Table 2: **Chemical Composition Sapodilla**[10]

Constituents	Approximate Amount
Moisture content % (w.b.)	73.37
Protein (g)	0.70
Fat (g)	1.10
Minerals (g)	0.05
Fiber (g)	2.60
Carbohydrates (g)	21.40
Energy (cal)	98.00
Phosphorous (mg)	72.00
Iron (mg)	1.25
Calcium (mg)	28.00
Thiamine (mg)	0.02
Riboflavin (mg)	0.03
Carotene (mg)	97.00
Ascorbic acid (mg)	0.06

[a] /100 g of edible portion

Table 3: Chemical Composition of Pineapple (*Ananas comosus*)[11]

Chemical composition of the edible portion of pineapple (all varieties) (the data from USDA Nutrient Database)

Nutrient	Units	Value per 100 grams
Proximates		
Water	g	86.00
Protein	g	0.54
Total lipid (fat)	g	0.12
Ash	g	0.22
Carbohydrate, by difference	g	13.12
Fiber, total dietary	g	1.4
Sugars, total	g	9.85
Sucrose	g	9.85
Glucose (dextrose)	g	5.99
Fructose	g	1.73
Vitamins		
Vitamin C, total ascorbic acid	mg	47.8
Vitamin A, IU	IU	58
Vitamin A, RAE	mcg_RAE	3
Other		
Carotene, beta	mcg	35

CHAPTER 3

CHARACTERIZATION OF HYDROGELS

3.1.Introduction:

Characterisation of polymers and modified polymers can be carried out by physical and chemical methods both in qualitative and quantitative manner.
In this chapter investigations of characterisation of hydrogels prepared in chapter 2 has been studied by FTIR ,SEM ,XRD methods. A brief introduction of these characterisation techniques is given below.

3.1.1Introduction of characterisation techniques:

3.1.1.1.Fourier transform infrared spectroscopy:

Infrared spectroscopy (IR spectroscopy) is the spectroscopy that deals with the infrared region of the electromagnetic spectrum. It covers a range of techniques, mostly based on absorption spectroscopy. It is used to identify and study chemicals. A common laboratory instrument that uses this technique is a Fourier transform infrared (FTIR) spectrometer.

The infrared portion of the electromagnetic spectrum consists the near-, mid- and far-infrared. The near-IR, approximately 14000–4000 cm^{-1} (0.8–2.5 μm wavelength) can excite overtone or harmonic vibrations. The mid-infrared, approximately 4000–400 cm^{-1} (2.5–25 μm) may be used to study the fundamental vibrations and associated rotational-vibrational structure. The far-infrared, approximately 400–10 cm^{-1} (25–1000 μm), lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy.

Fourier transform infrared spectroscopy (**FTIR**)[(1)] is a technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas. An FTIR spectrometer simultaneously collects spectral data in a wide spectral range while dispersive spectrometer measures intensity over a narrow range of wavelengths at a time. The term *Fourier transform infrared spectroscopy* originates from the fact that a Fourier transform (a mathematical algorithm) is required to convert the raw data into the actual spectrum

The first low-cost spectrophotometer capable of recording an infrared spectrum was

the Perkin-Elmer Infracord produced in 1957[(2)] .

3.1.1.1.1. FTIR interferogram:

This is the "raw data" which can be Fourier transformed into the FTIR spectrum Fourier transform spectroscopy is a less intuitive way to obtain the same information.

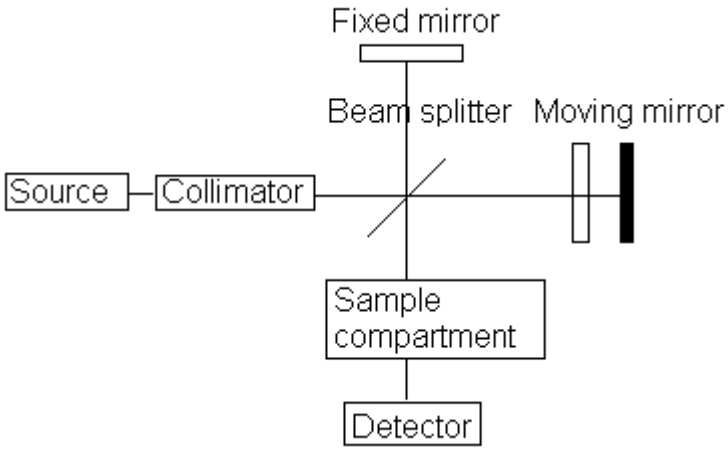
It uses a Michelson interferometer, that allows some wavelengths to pass through but blocks others (due to wave interference. The processing required turns out to be a

common algorithm called the Fourier transform (hence the name, "Fourier transform spectroscopy"). The raw data is sometimes called an "interferogram".

Thermo **Scientific** Nicolet 380 **FT-IR Spectrometer**

3.1.1.1.2.Michelson interferometer:

Schematic diagram of a Michelson interferometer, configured for FTIR:



3.1.1.1.3.Resolution: The spectral resolution in wavenumbers per cm is equal to the reciprocal of the maximum retardation in cm.

The throughput advantage is important for high-resolution FTIR as the monochromator in a dispersive instrument with the same resolution would have very narrow entrance and exit slits.

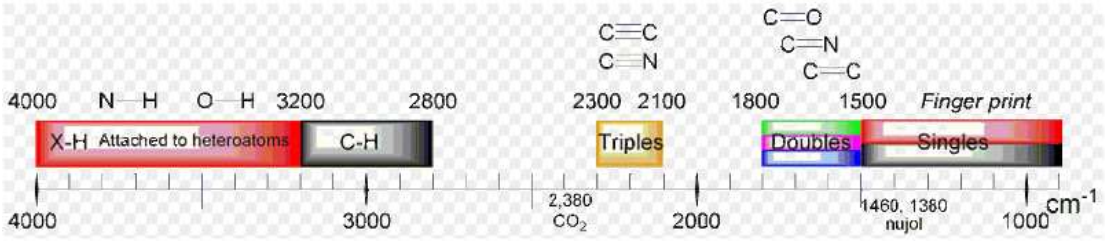
3.1.1.1.4. Beam splitter:

A thin film, usually of a plastic material, is used as beam splitter.

3.1.1.1.5. Fourier transform:

The interferogram in practice consists of a set of intensities measured for discrete values of retardation thus, a discrete Fourier transform is needed.

3.1.1.1.6. IR FREQUENCIES

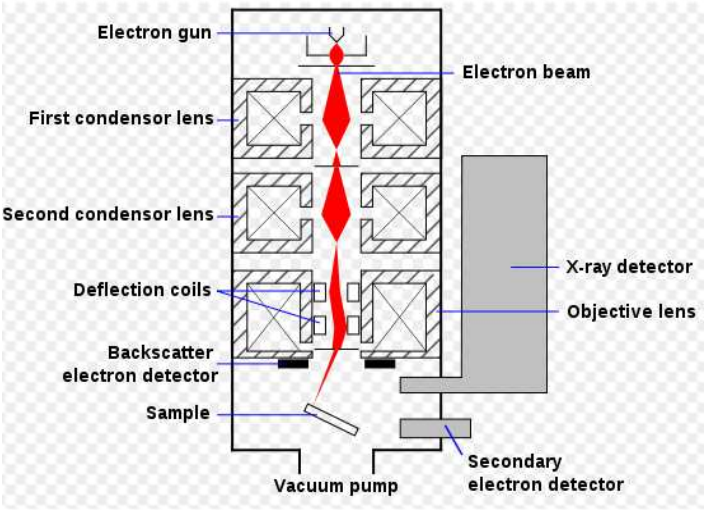


3.1.1.2.Scanning Electron Microscope (**SEM**):

A **scanning electron microscope** (**SEM**) is a type of electron microscope that images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition, and other properties such as electrical conductivity. The first SEM image was obtained by Max Knoll, who in 1935 obtained an image of silicon steel showing electron channeling contrast.[3] The types of signals produced by an SEM include secondary electrons, back-scattered electrons (BSE), characteristic X-rays, light (cathodoluminescence), specimen current and transmitted electrons. The signals result from interactions of the electron beam with atoms at or near the surface of the sample. Because the intensity of the BSE signal is strongly related to the atomic number (Z) of the specimen, BSE images can provide information about the distribution of different elements in the sample. Characteristic X-rays are emitted when the electron beam removes an inner shell electron from the sample, causing a higher energy electron to

fill the shell and release energy. These characteristic X-rays are used to identify the composition and measure the abundance of elements in the sample.

SEM opened sample chamber[10]



Schematic diagram of SEM[10]

S-3700 N M ODEL FOR SEM BY HITACHI[(10A)]

3.1.1.2.1.Scanning process and image formation :

In a typical SEM, an electron beam is thermionically emitted from an electron gun fitted with a tungsten filament cathode. Other types of electron emitters include lanthanum hexaboride (LaB_6) cathodes. The electron beam, which typically has an energy ranging from 0.5 keV to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the *x* and *y* axes so that it scans in a raster fashion over a rectangular area of the sample surface. When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 µm into the surface. The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering. The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current. Electronic amplifiers of various types are used to amplify the signals which are displayed as variations in brightness on a cathode ray tube. The raster scanning of the CRT display is synchronised with that of the beam on the specimen in the microscope, and the resulting image is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen. The image is digitally captured and displayed on a computer monitor and saved to a computer's hard disk.

3.1.1.2.2. Sample preparation:

All samples must also be of an appropriate size to fit in the specimen chamber and are generally mounted rigidly on a specimen holder called a specimen stub. For conventional imaging in the SEM, specimens must be electrically conductive at the surface, and electrically grounded to prevent the accumulation of electrostatic charge at the surface. Metal objects require little special preparation for SEM except for cleaning and mounting on a specimen stub. Nonconductive specimens are usually coated with an ultrathin coating of electrically-conducting material, commonly gold, deposited on the sample either by low vacuum sputter coating or by high vacuum evaporation. Conductive materials in current use for specimen coating include gold, gold/palladium alloy, platinum, osmium,[4] iridium, tungsten, chromium and graphite. Two reasons for coating, even when there is enough specimen conductivity to prevent charging, are to increase signal and surface resolution, especially with samples of low atomic number (Z) and improvement in resolution arises because backscattering and secondary electron emission near the surface are enhanced and thus an image of the surface is formed. An alternative to coating for some biological samples is to increase the bulk conductivity of the material by impregnation with osmium using variants of the OTO staining method (O-osmium, T-thiocarbohydrazide, O-osmium.[5,6] For SEM, a specimen is normally required to be completely dry, since the specimen chamber is at high vacuum. Low-temperature scanning electron microscopy is applicable to the imaging of temperature-sensitive materials such as ice[7,8]. and fats.[9]

3.1.1.2.3Materials:

Geological specimens that undergo WDS or EDS analysis are often carbon coated. Metals are not generally coated prior to imaging in the SEM because they are conductive and provide their own pathway to ground. Metals, geological specimens, and integrated circuits all may also be chemically polished for viewing in the SEM.

3.1.1.3.XRD Patterns :

X-radiation (composed of X-rays) is a form of electromagnetic radiation. X-rays have a wavelength in the range of 0.01 to 10 nanometers . X- RAY machines were introduced in 1974 by Samuel Eilenberg[11].

X-ray powder diffraction is a non-destructive technique[12] widely applied for the characterisation of crystalline materials. The method has been traditionally used for phase identification, quantitative analysis and the determination of structure imperfections. Now applications have been extended to new areas, such as the determination of crystal structures and the extraction of three-dimensional microstructural properties. Various kinds of micro- and nano-crystalline materials can be characterised from X-ray powder diffraction, including inorganics, organics, drugs, minerals, zeolites, catalysts, metals and ceramics.

The observed diffraction line profiles in a powder diffraction pattern are distributions of intensities I(2θ) defined by several parameters: (i) the reflection angle *position* $2\theta_0$ at the maximum intensity (related to the lattice spacing *d* of the diffracting *hkl* plane

and the wavelength λ by Bragg.s law, λ = 2*d* sinθ), (ii) the *dispersion* of the distribution, full-width at half-maximum and integral breadth, (iii) the line *shape factor*, and (iv) the *integrated intensity* (proportional to the square of the structure factor amplitude). The specific applications derivedfrom each of them have been listed as ;

3.1.1.3.1.Diffraction Line parameter with Applications

3.1.1.3.1.1.Peak position: Unit-cell parameter refinement, pattern indexing, space group determination ($2\theta_0$/absent reflections) **,** anisotropic thermal expansion, macrostress: sin2ψ method and phase identification (*d*/*I*).

3.1.1.3.1.2.Intensity: Phase abundance, Reaction kinetics, Crystal structure analysis (whole pattern), Rietveld refinement (whole pattern) search/match, Phase identification, preferred orientation, texture analysis.

3.1.1.3.1.3.Width/breadth and shape: Instrumental resolution function microstructure: line profile analysis microstructure (crystallite size, size distribution, lattice distortion, structure mistakes, dislocations, composition gradient), crystallite growth kinetics three-dimensional microstructure (whole pattern).

3.1.1.3.1.4.Non-ambient and dynamic diffraction: *in situ* diffraction under external constraints reaction kinetics

3.1.1.3.1.5.Application of X-RAY detecting Polymer crystallinity : A polymer can be considered partly crystalline and partly amorphous. The crystalline domains act as a reinforcing grid, like the iron framework in concrete, and improves the performance over a wide range of temperature. However, too much crystallinity causes brittleness. The crystallinity parts give sharp narrow diffraction peaks and the amorphous component gives a very broad peak (halo)[13]. The ratio between these intensities can be used to calculate the amount of crystallinity in the material.

x-ray machine[14] D8-BRUKER

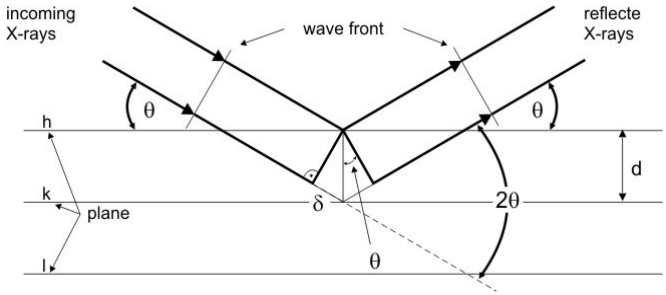
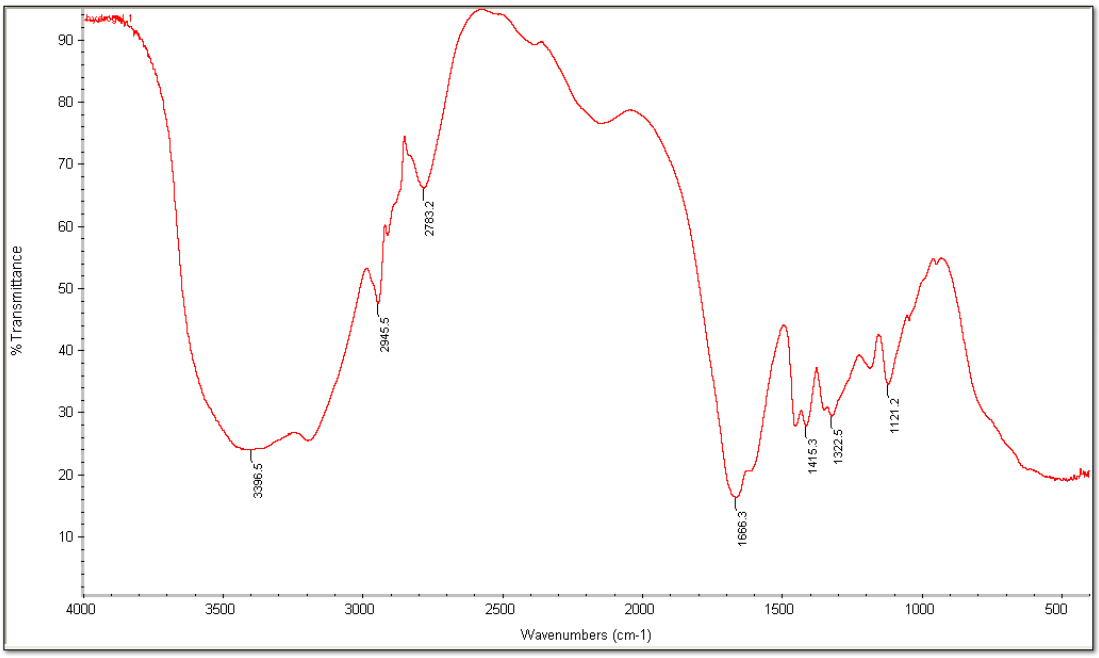
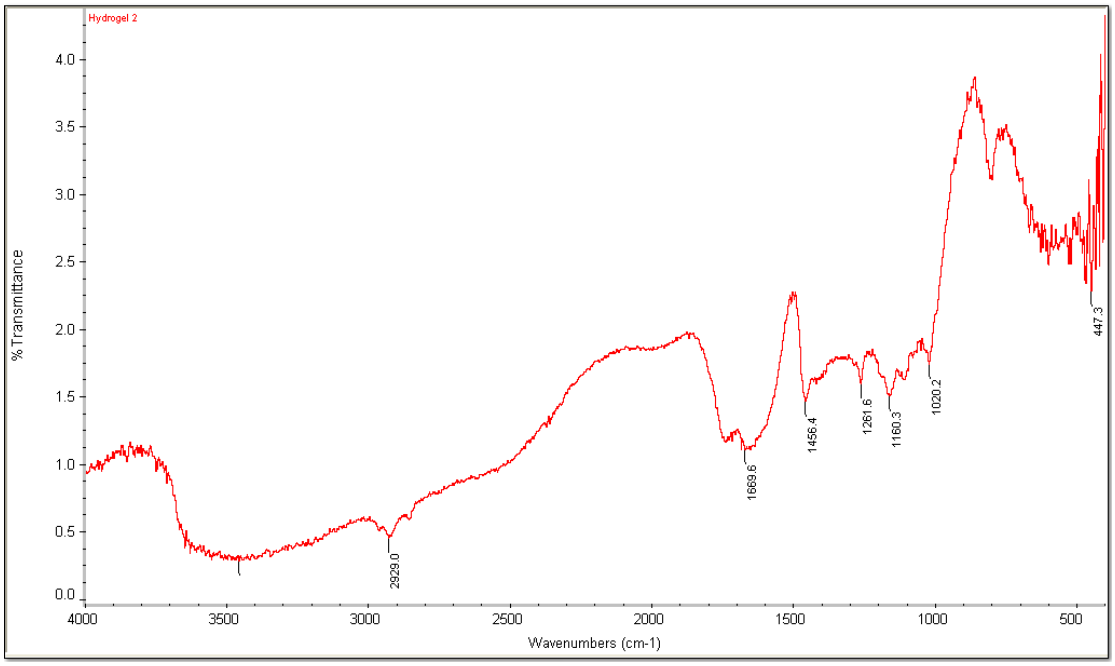


Fig: Showing parameters of XRD[15]

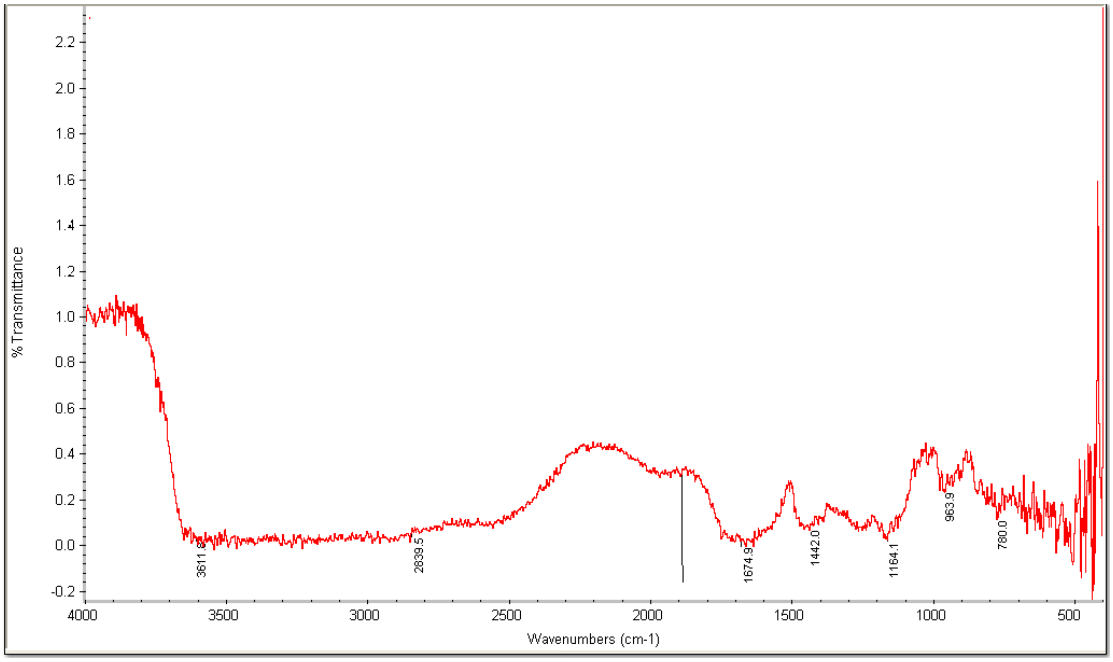
3.2.FTIR OF HYDROGELS



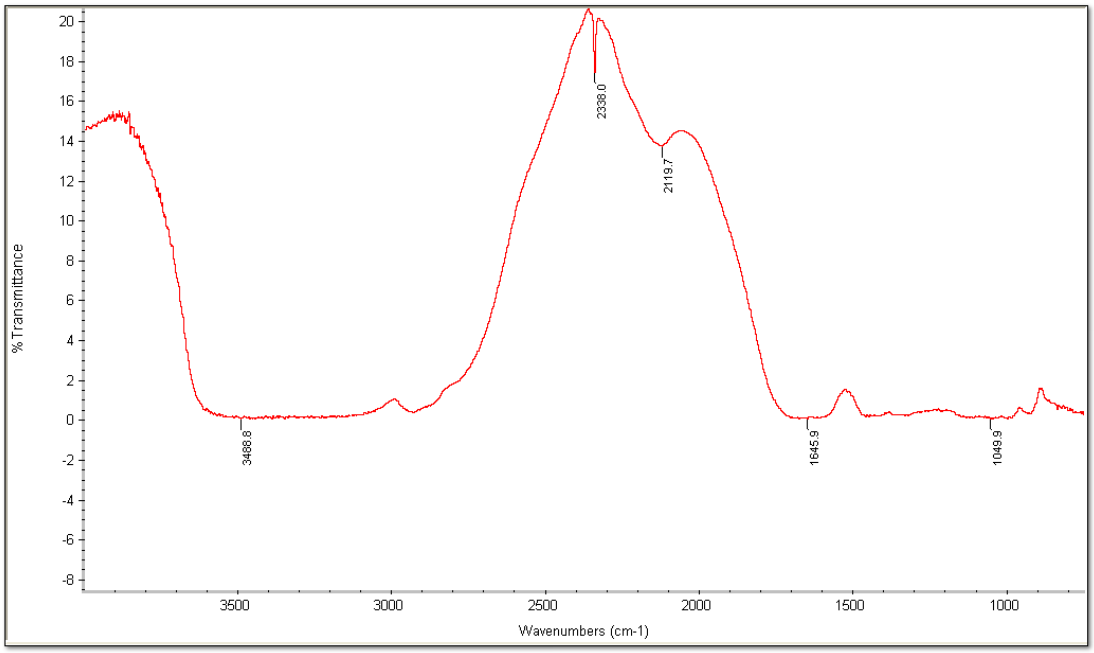
3.2.1.FTIR OF HYDROGEL 1



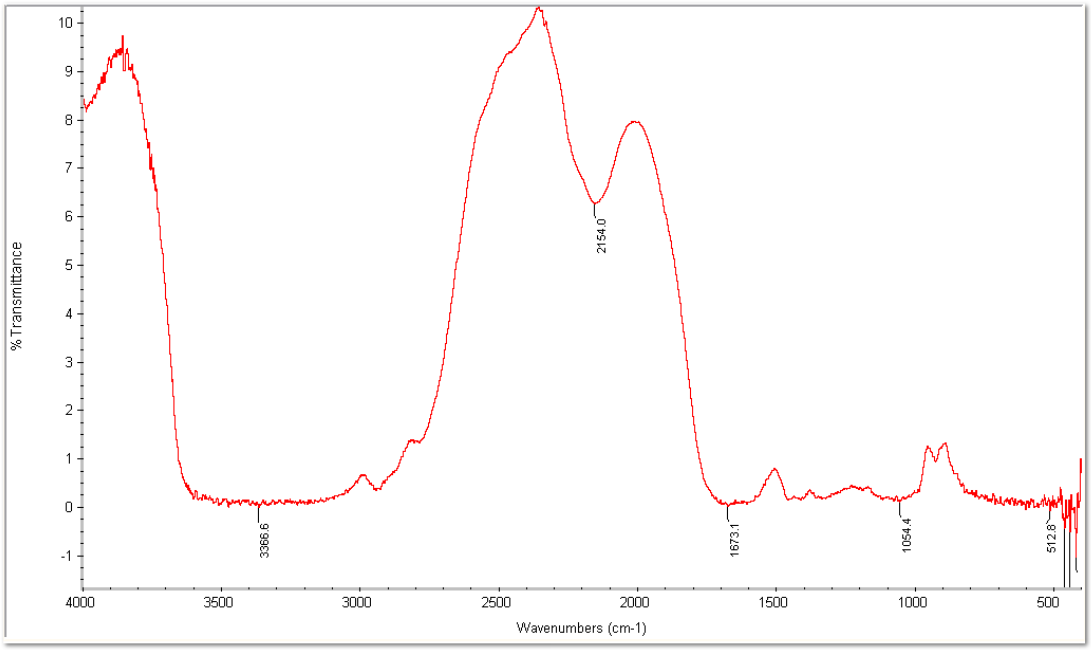
3.2.2.FTIR OF HYDROGEL 2



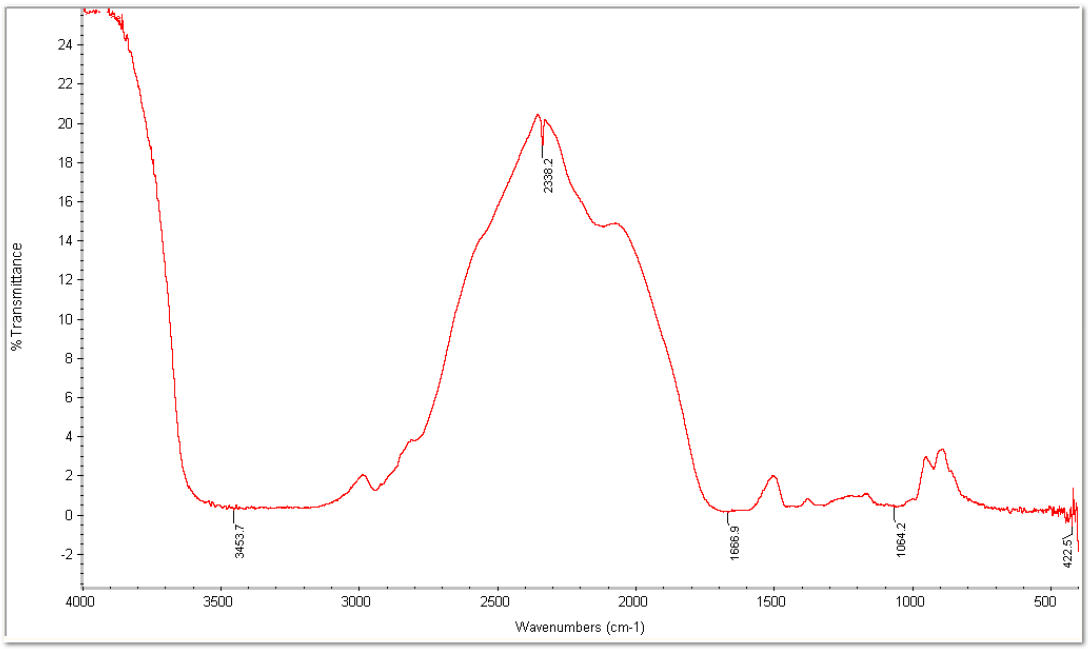
3.2.3.FTIR OF HYDROGEL 3



3.2.4.FTIR OF HYDROGEL 4

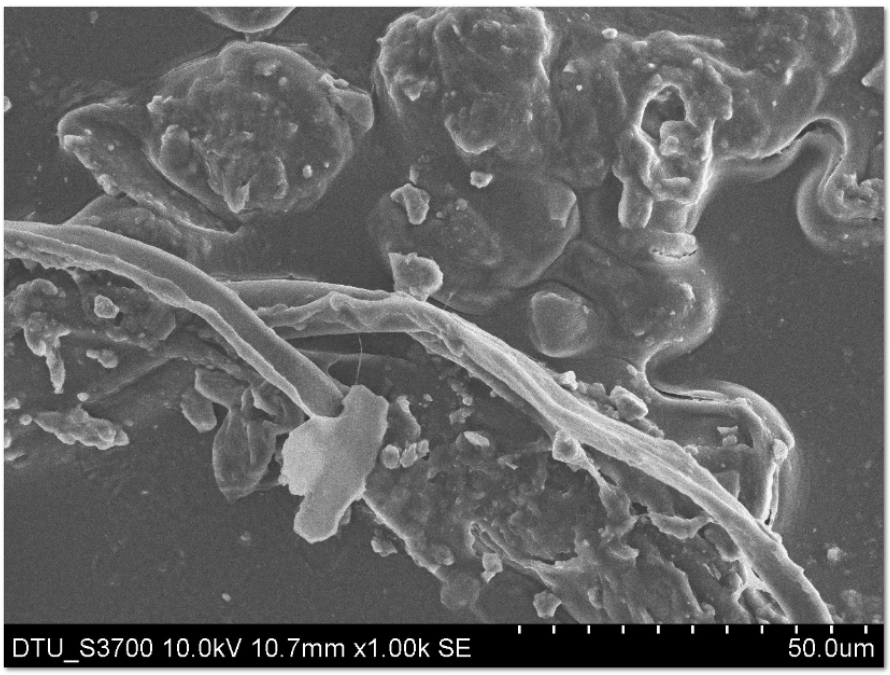


3.2.5.FTIR OF HYDROGEL 5

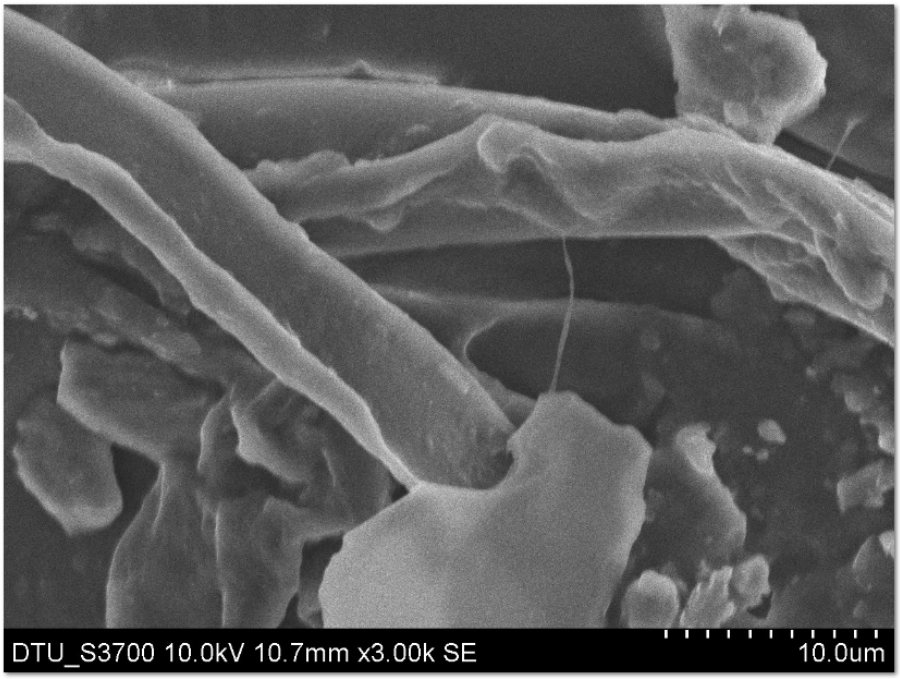


3.2.6.FTIR OF HYDROGEL 6

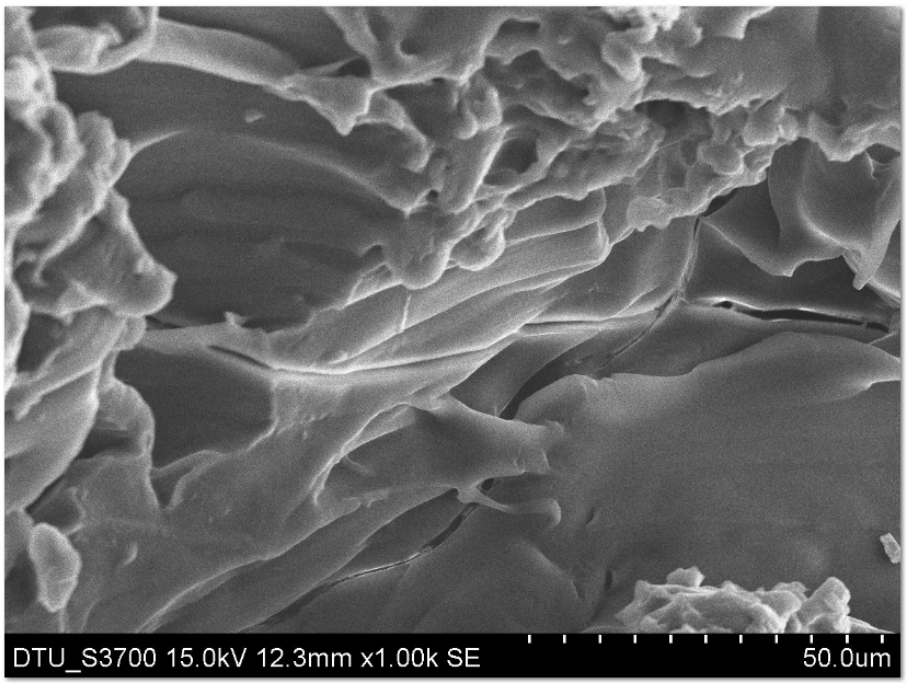
3.3.SEM IMAGE OF HYDROGELS



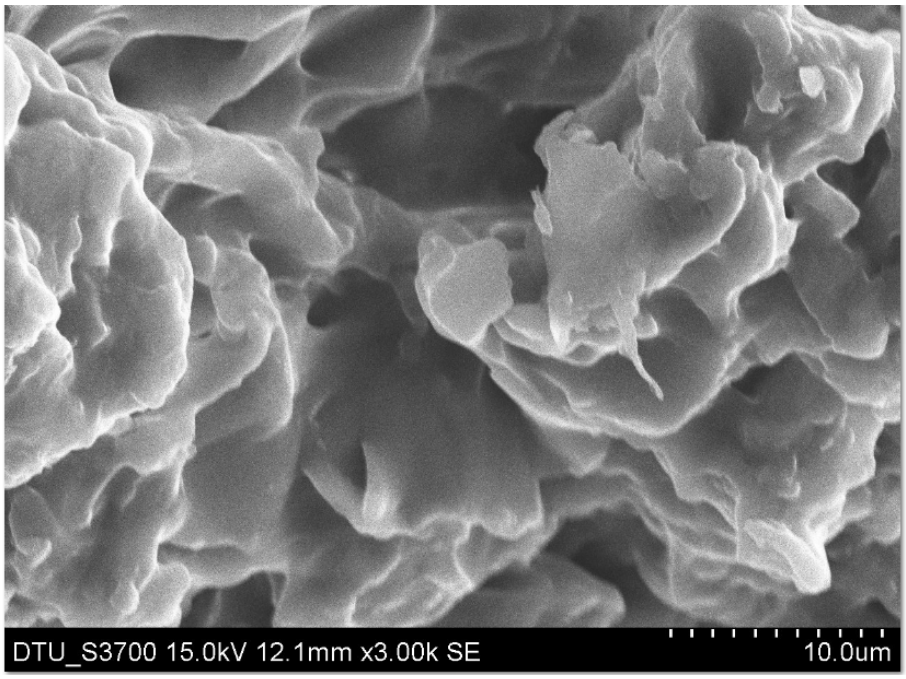
3.3.1.1.SEM IMAGE OF HYDROGEL 1(A)



3.3.1.2.SEM IMAGE OF HYDROGEL 1(B)



3.3.2.1SEM IMAGE OF HYDROGEL 2(A)



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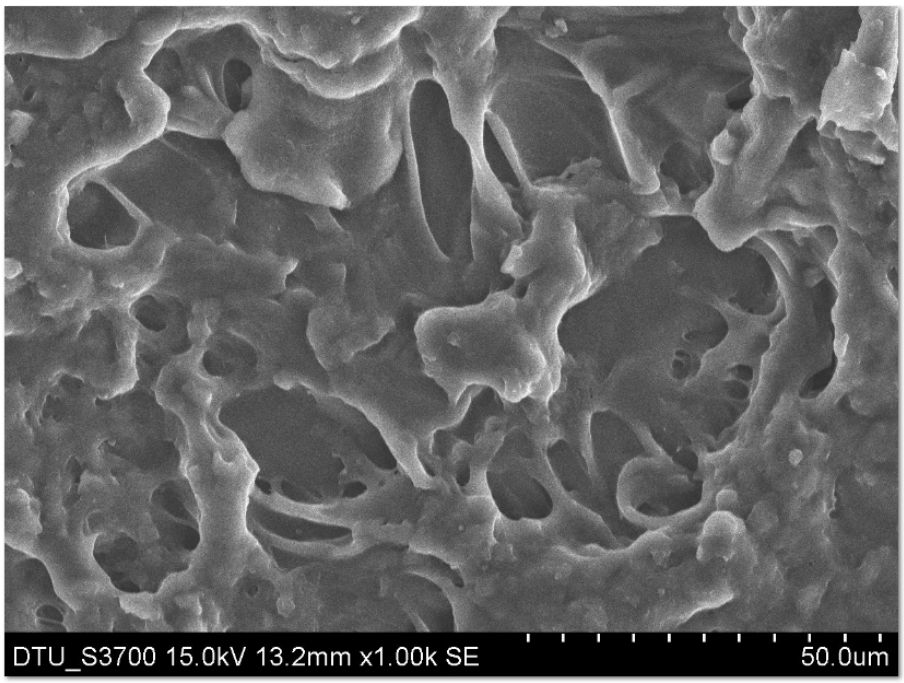
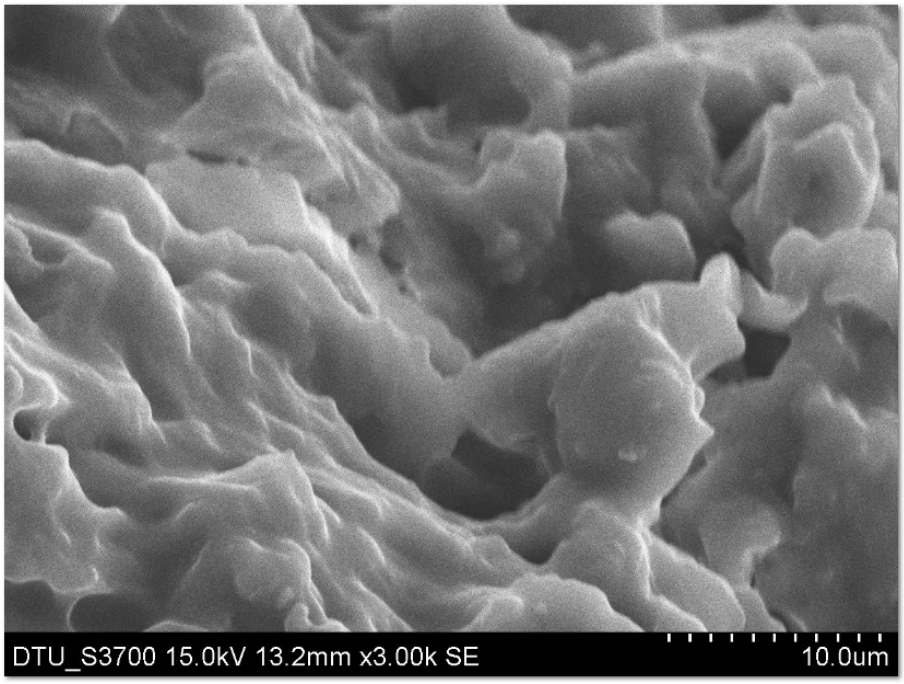


3.3.3.1.SEM IMAGE OF HYDROGEL3 (A)



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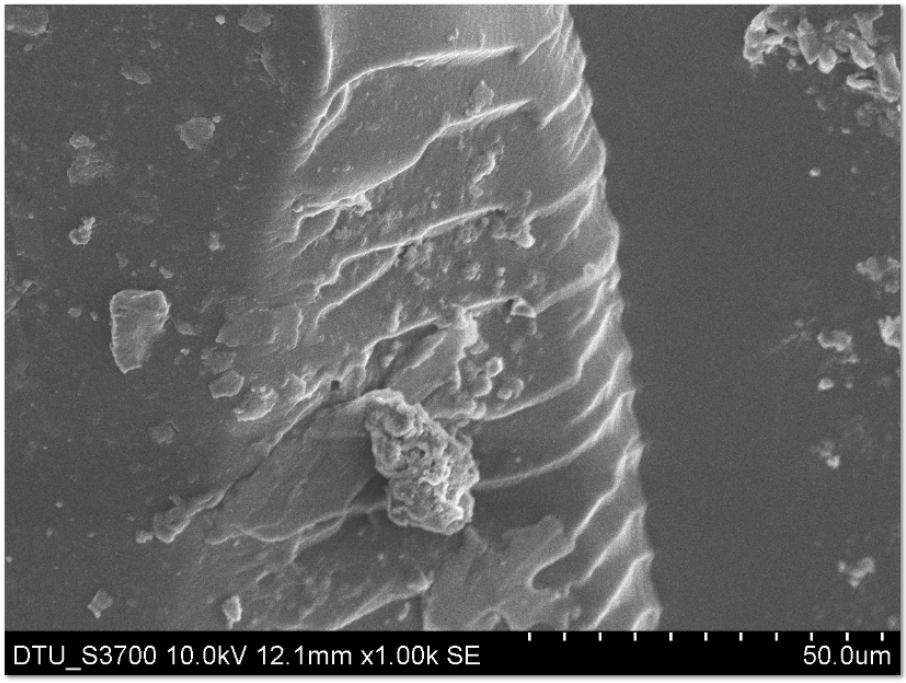
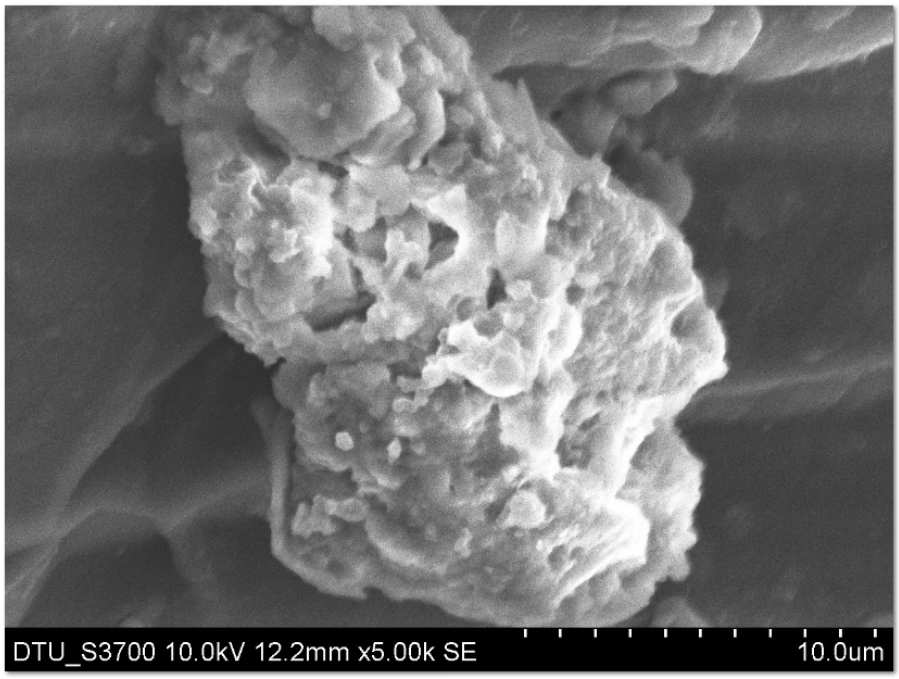
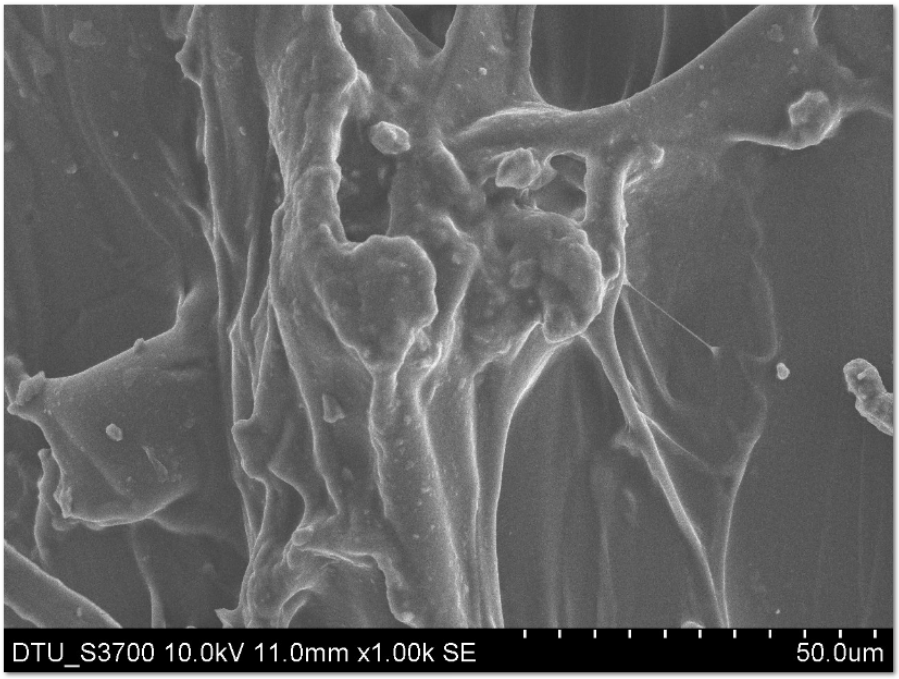


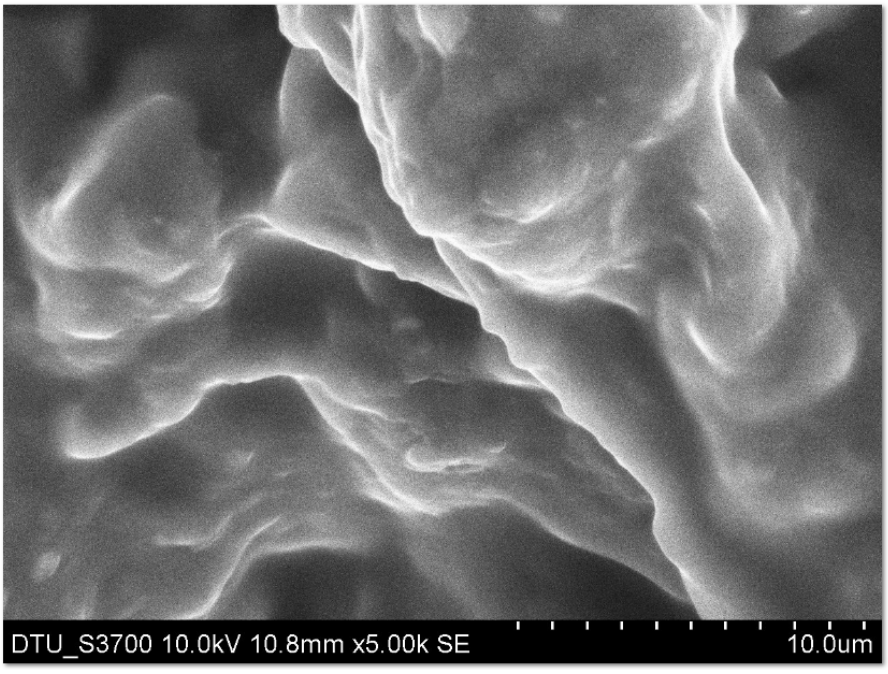
3.3.4.1.SEM IMAGE OF HYDROGEL4 (A)



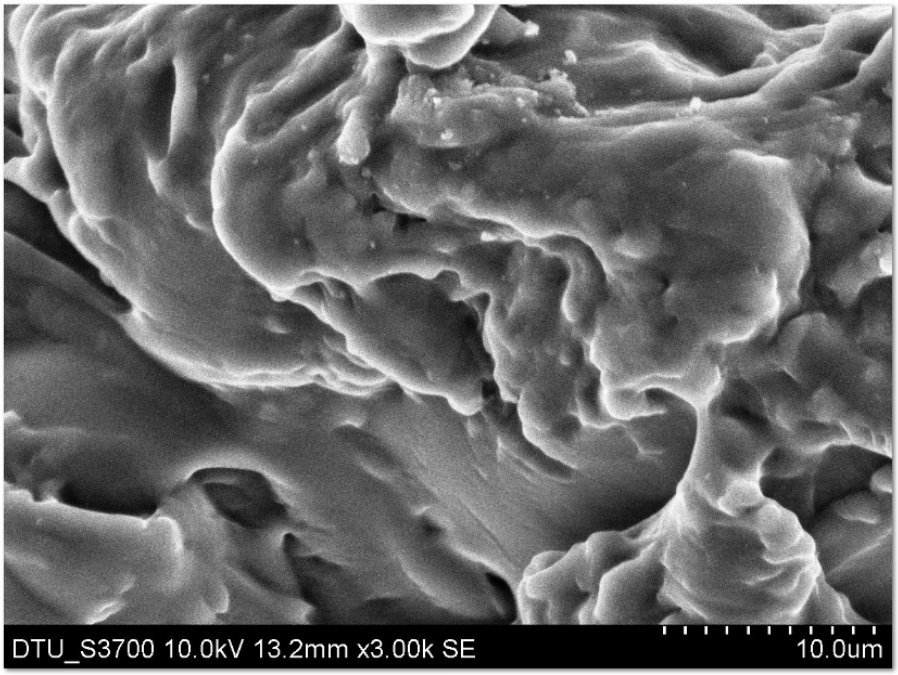
3.3.4.2.SEM IMAGE OF HYDROGEL4 (B)



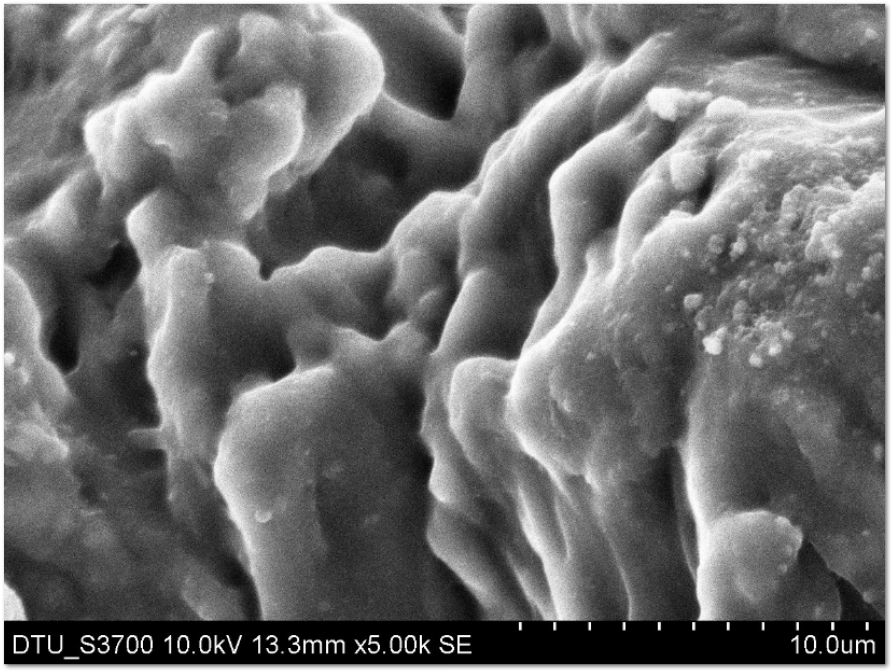
3.3.5.1.SEM IMAGE OF HYDROGEL5 (A)



3.3.5.2.SEM IMAGE OF HYDROGEL5 (B)

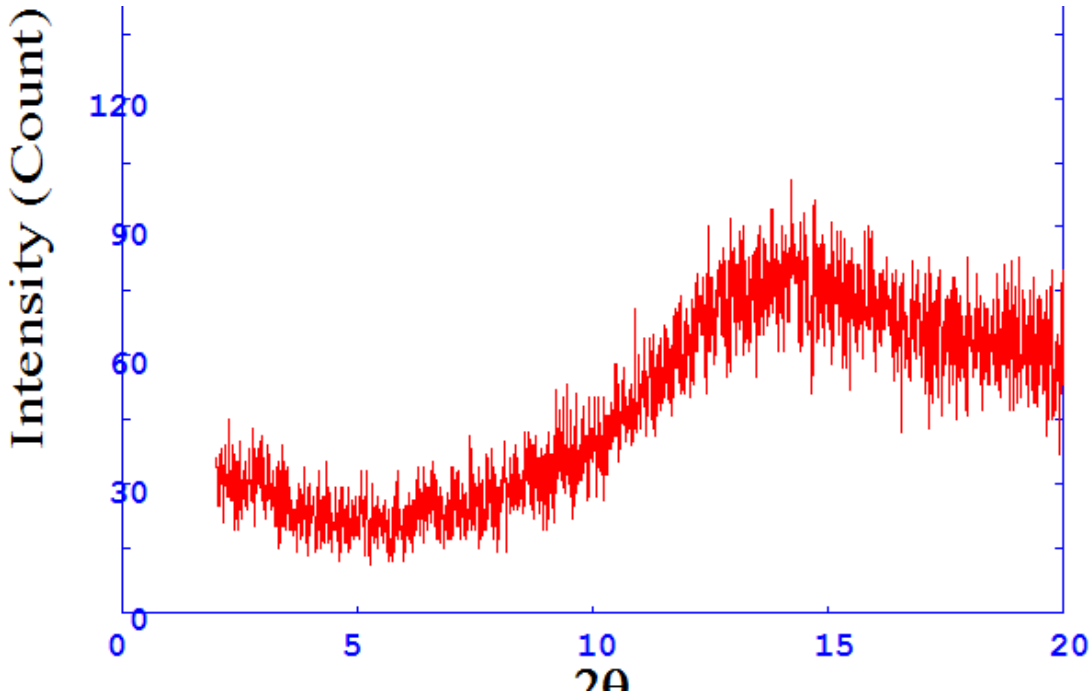


3.3.6.1.SEM IMAGE OF HYDROGEL6 (A)

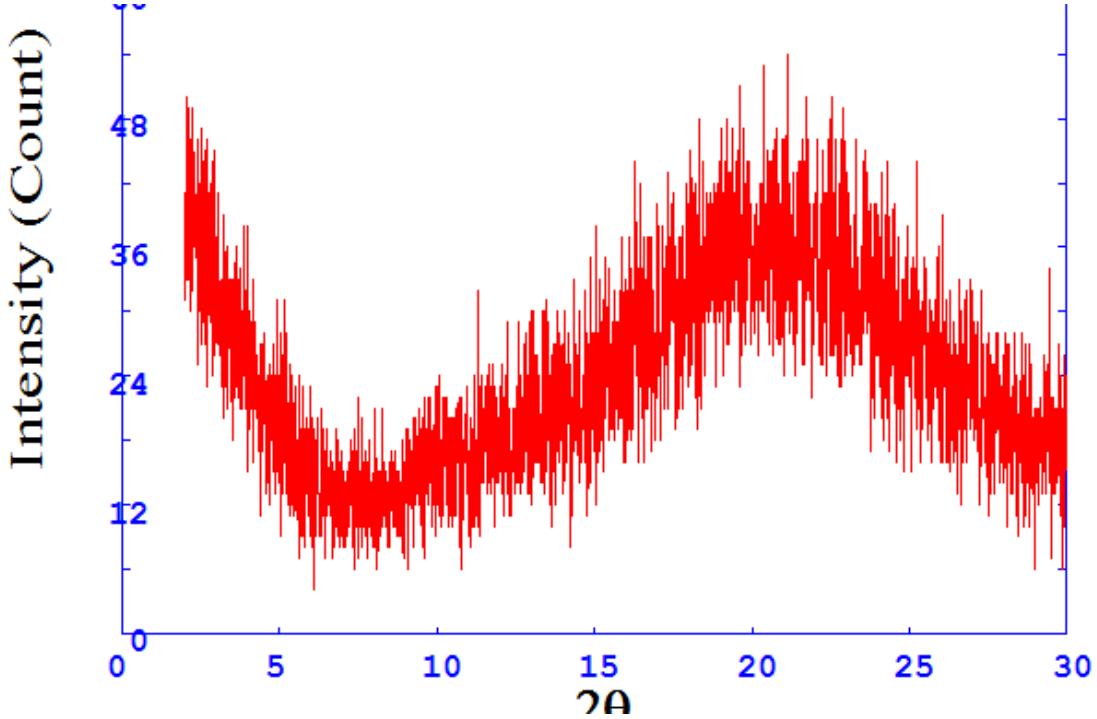


3.3.6.2.SEM IMAGE OF HYDROGEL6 (B)

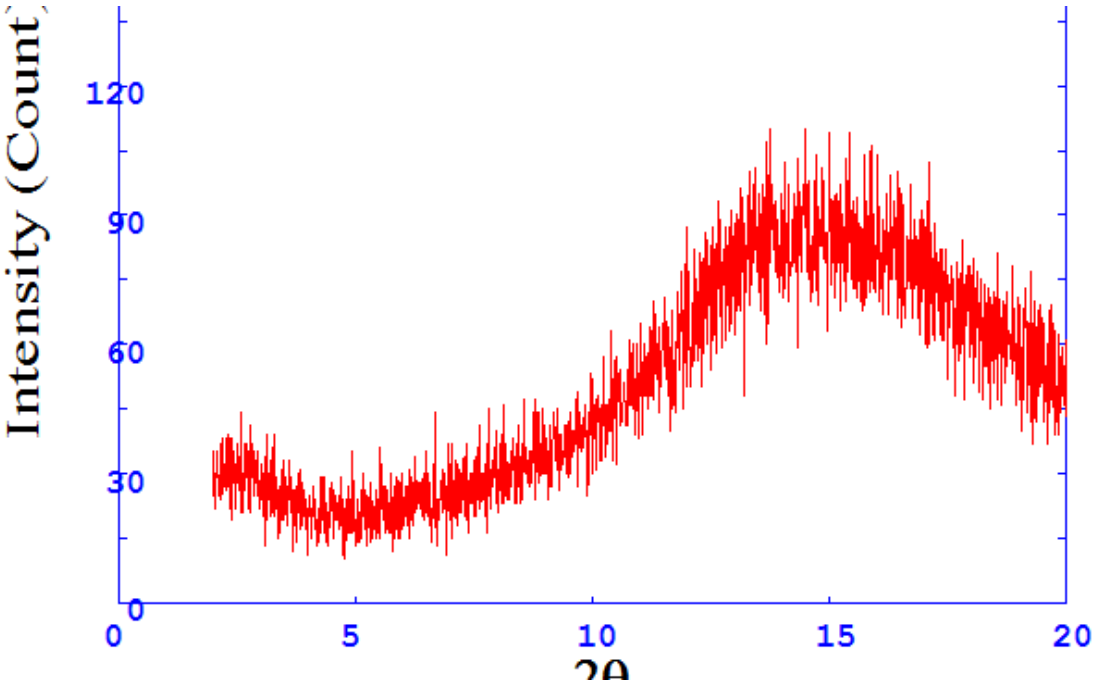
3.4.XRD OF HYDROGELS



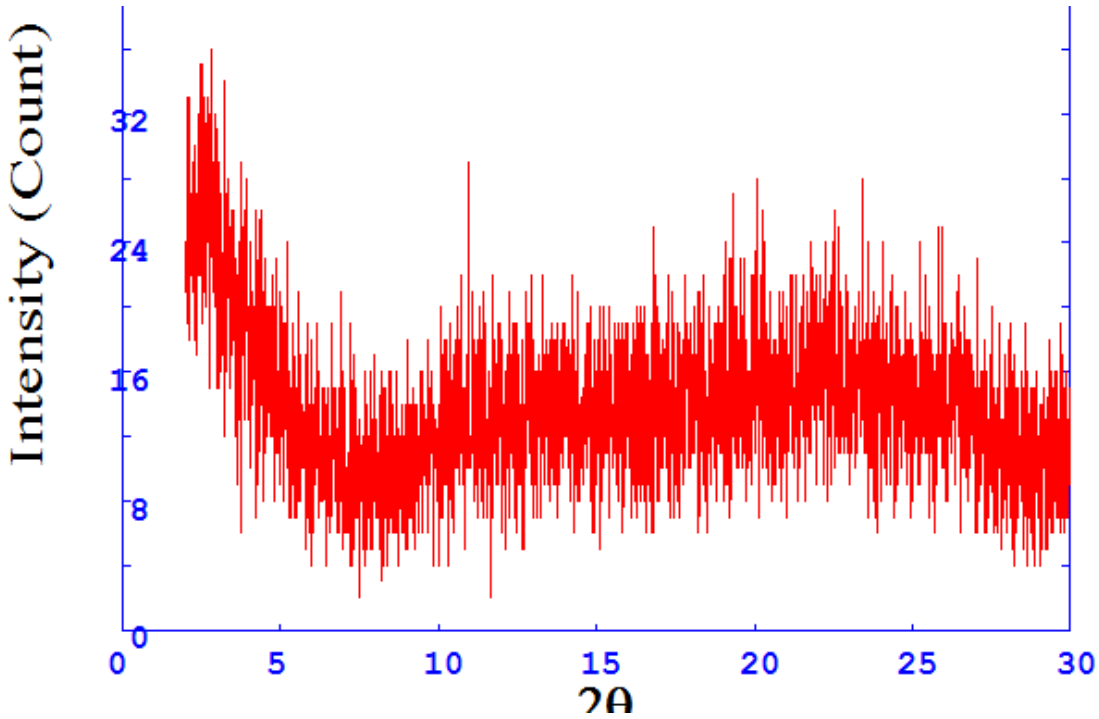
3.4.1.XRD OF HYDROGEL 1



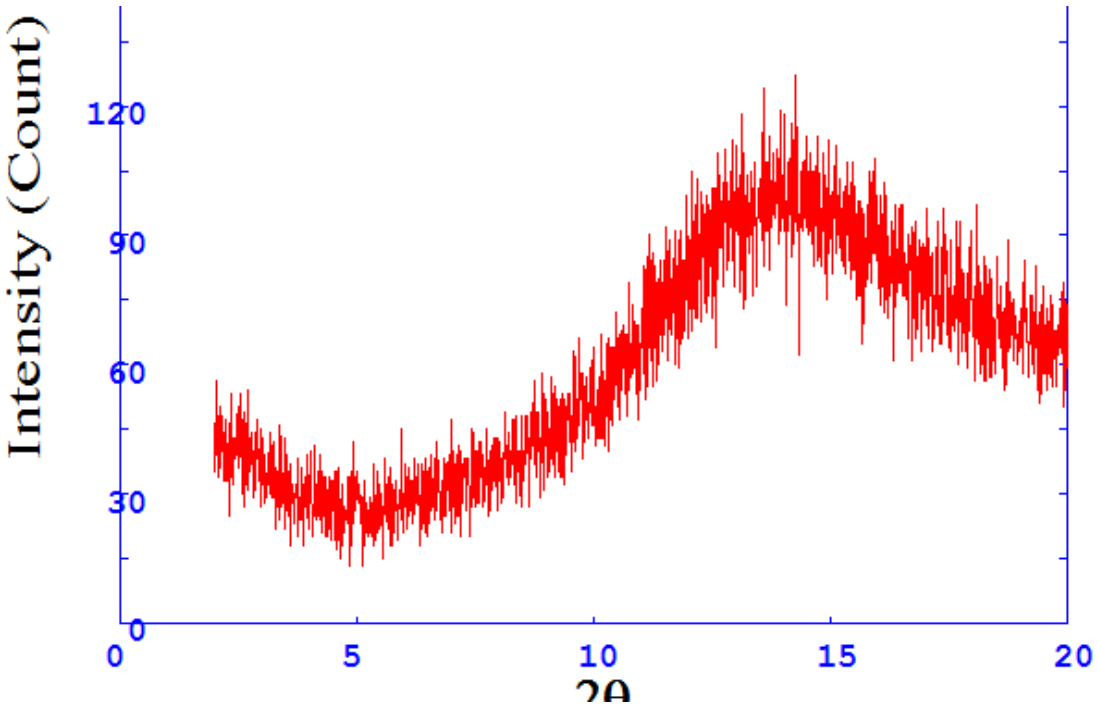
3.4.2.XRD OF HYDROGEL 2



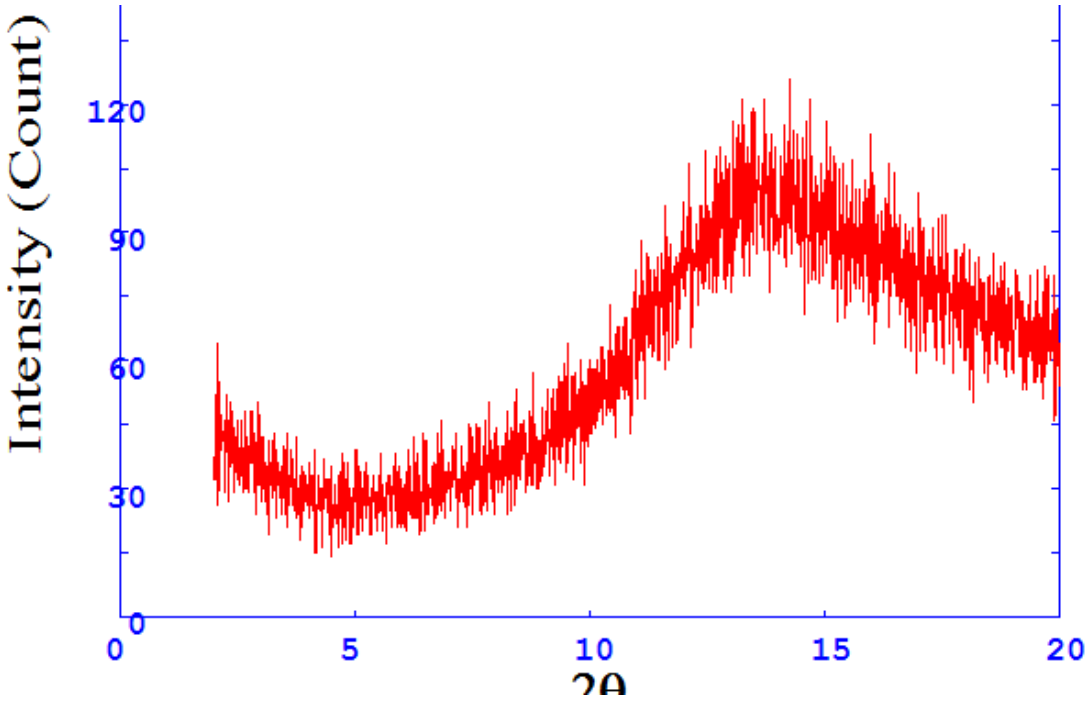
3.4.3.XRD OF HYDROGEL3



3.4.4.XRD OF HYDROGEL4



3.4.5.XRD OF HYDROGEL5



3.4.6.XRD OF HYDROGEL 6

3.5.Experimental :

FTIR , SEM and XRD Studies of Hydrogels :

3.5.1.FTIR:

FTIR measurements of various hydrogels including Polyacrylamide and its copolymers were performed using Thermo Scientific Nicolet 380 FT-IR Spectrometer. Samples were thoroughly grounded mixed with KBr. The mixture was compressed to prepare a pellet for FTIR analysis. FTIR spectra were recorded in the range from 4000 to 500 cm^{-1}

3.5.2.SEM:

SEM of hydrogel samples were recorded on Hitachi(S- 3700N) .All samples were gold coated prior to measurement.

3.5.3.XRD:

XRD hydrogels were recorded on D8-BRUKER (Between 2 to 20^0 At .5 degree per minutes).

3.6.Result and Discussion

3.6.1.FTIR of Hydrogels

3.6.1.1.FTIR of Hydrogel 1:

=>Two bands between 3100-3500 cm^{-1} corresponds to -N-H stretching of amide group.

=> The peak at 2945.5 cm^{-1} corresponds to $>CH_2$ asymmetric stretching of carbon chain.

=> The strong peak at 1666.3 cm^{-1} corresponds to >C=O stretching of amide group.

=> The strong peak at 1415.3 cm^{-1} corresponds to -C-H bending.

=> The peak at1322.5cm^{-1} corresponds to C-H in plane bending; corresponds to unreacted monomer (acrylamide).

=> The peak at1121.2 cm^{-1}corresponds to –C-C=O (C-C) stretching.

3.6.1.2.FTIR of Hydrogel 2:

=>Broad band between2400-3400cm^{-1}corresponds to –O-H stretching hydrogen bonded. It supports the presence of –COOH group from acrylic acid.

=> Peak at 2929 cm^{-1}shows the presence of –C-H stretching in polymer backbone.

=> Peak at 1669.6 cm^{-1} shows the presence of >C=O stretching of amide group.

=> Peak at 1456.4 cm^{-1} corresponds to -C-H bending.

=> Peak at 1261.6cm^{-1} corresponds to –C-O (-COOH) stretching.

3.6.1.3.FTIR of Hydrogel 3:

=>Broad band between 2400-3400 cm^{-1}corresponds to –O-H stretching hydrogen bonded. It supports the presence of –COOH group from acrylic acid.

=> Peak 1674.9 cm^{-1} shows the presence of >C=O stretching of amide group.

=> Peak at 1442cm^{-1} shows the presence –O-H bending of carboxylic acid group.

=> The peak at1164.1 cm^{-1}corresponds to –C-C=O (C-C) stretching.

3.6.1.4.FTIR of Hydrogel 4:

=>Broad band between 3200-3600 cm^{-1}corresponds to –O-H stretching hydrogen bonded. It supports the presence of –OH group from sugar.

=> Peak 1645.9 cm^{-1} shows the presence of >C=O stretching of amide group.

=> Peak at1049.9 cm^{-1}corresponds to-C-O stretching.

=>The IR band at2338 cm^{-1}, which may corresponds to adsorbed CO_2[16]

=>The IR band at2119,7 cm^{-1}, which may corresponds to nitrile .It seems to be an error.

3.6.1.5.FTIR of Hydrogel 5:

=>Broad band between 3200-3600 cm^{-1}corresponds to –O-H stretching hydrogen bonded. It supports the presence of –OH group from sugar.

=> Peak 1673.1 cm^{-1} shows the presence of >C=O stretching of amide group.

=> Peak at1054.4 cm^{-1}corresponds to-C-O stretching.

=>The IR band at2154 cm^{-1}, which may corresponds to adsorbed CO[17]

3.6.1.6.FTIR of Hydrogel 6:

=>Broad band between 3200-3600 cm^{-1}corresponds to –O-H stretching hydrogen bonded. It supports the presence of –OH group from sugar.

=> Peak 1666.9 cm^{-1} shows the presence of >C=O stretching of amide group.

=> Peak at1064.2 cm^{-1}corresponds to-C-O stretching.

=>The IR band at2338.2 cm^{-1}, which may corresponds to adsorbed CO_2[16]

3.6.2.SEM of HYDROGELS

3.6.2.1.SEM of HYDROGEL 1:

From SEM image 1(a) & 1(b); it clear that surface of hydrogel of polyacrylamide is not plane and smooth ;it rough and there are some space where water is entrapped. FIG 1(a) is at 1K and FIG 1(b) is at 3K; on increasing magnification it is seen that material is having surface like sponge.

3.6.2.2.SEM of HYDROGEL 2:

From SEM image 2(a) & 2(b); it clear that surface of hydrogel of poly(acrylamide-co-acrylicacid) is discontinuous but smooth. FIG 2(a) is at 1K and FIG 2(b) is at 3K.It seems more dense in comparision to hydrogel of polyacrylamide. Surface is having no pores. That is the reason; it is not swelling much. Observed % of swelling is lower in comparision to hydrogel 1.

3.6.2.3.SEM of HYDROGEL 3:

From SEM images 3(a) & 3(b); it clear that surface of hydrogel of poly(acrylamide-co-meth acrylic acid) is discontinuous but smooth. FIG 3(a) is at 1K and FIG 3(b) is at 3K.It seems more dense in comparision to hydrogel of polyacrylamide. Surface is having no pores. That is the reason; it is not swelling much. Observed % of swelling is lower in comparision to hydrogel 1.

3.6.2.4.SEM of HYDROGEL 4:

From SEM image 4(a); it clear that surface of hydrogel of poly(acrylamide-co-cane juice) is continuous but rough. FIG 4(a) is at 1K and FIG 4(b) is at 5K. From FIG 4(b); it is clear that there are some pores on surface i.e., it is swelling much. From FIG 4(a); surface seems like sand; in which water can penetrate easily.

3.6.2.5.SEM of HYDROGEL 5:

FIG 5(a) is at 1K and FIG 5(b) is at 5K. From FIG 5(a); it is clear that there is something film like structure on the surface of poly(acrylamide-co-sapodilla extract) hydrogel; which is quite smooth. It is also seen that surface is having some tack. From FIG 5(b); it is seen that material is sponge like and can be easily swelled.

3.6.2.6. SEM of HYDROGEL 6:

FIG 6(a) is at 3K and FIG 6(b) is at 5K. From SEM images of poly(acrylamide-co-pine apple juice) hydrogel; it is clear that surface is quite rough. Some small particles in discontinuous manner are also seen on the surface. SEM image shows that material is easily penetrable. This is the reason quite swelling is observed.

3.6.3.XRD OF HYDROGELS

3.6.3.1.X ray of Hydrogel 1:

From X-ray data of hydrogel 1; it is clear that material is amorphous in nature as no sharp peak is detected in data.

3.6.3.2.X ray of Hydrogel 2:

From X-ray data of hydrogel 2; it is clear that material is amorphous in nature as a broad peak is detected in data. From the data it is also clear that hydrogel of copolymer of Acrylamide with Acrylic acid is slightly more crystalline than that of polyacrylamide; as peak is lesser broad in this case than that of hydrogel 1.

3.6.3.3.X ray of Hydrogel 3:

From X-ray data of hydrogel 3; it is clear that material is amorphous in nature as a broad peak is detected in data. From the data it is also clear that hydrogel of copolymer of acrylamide with Meth acrylic acid is slightly more crystalline than that of polyacrylamide; as peak is lesser broad in this case than that of hydrogel 1.

3.6.3.4.X ray of Hydrogel 4:

From X-ray data of hydrogel 4; it is clear that material is amorphous in nature as no sharp peak is detected in data. It is more amorphous than that of hydrogel 1 as in present case only background is found.

3.6.3.5.X ray of Hydrogel 5:

From X-ray data of hydrogel 5; it is clear that material is amorphous in nature as a broad peak is detected in data. From the data it is also clear that hydrogel of copolymer of acrylamide with sapodilla extract is slightly more

crystalline than that of polyacrylamide; as peak is lesser broad in this case than that of hydrogel 1. It is also more crystalline than hydrogel of acrylamide and cane juice.

3.6.3.6.X ray of Hydrogel 6:

From X-ray data of hydrogel 6; it is clear that material is amorphous in nature as a broad peak is detected in data. From the data it is also clear that hydrogel of copolymer of acrylamide with pineapple juice is slightly more crystalline than that of polyacrylamide; as peak is lesser broad in this case than that of hydrogel 1. It is also more crystalline than hydrogel of acrylamide and cane juice.

CHAPTER 4

Swelling Study of Hydrogel

4: Swelling Study

4.1.Introduction:

Hydrogels are polymers characterised by their hydrophilicity, insolubility and responsiveness to swelling in water .They swell to an equilibrium volume and preserve their shape. Hydrophilicity is due to presence of –OH , -COOH , $-SO_3H$ and $-CONH_2$ groups or their derivatized salt forms .The stability of shape and insolubility is due to the presence of three- dimensional network .The tendency of such networks in dry state to get solvated is referred as high free energy network or hungry networks[1-3] Balance between cohesive and dispersive forces in swollen state is responsible for properties of gels .Cohesive forces can be covalent [4] electrostatic , hydrophobic or dipole- dipole interactions[5,6] . Imbibing large amount of water by hydrogel results in their poor mechanical properties.[7] However some natural hydrogels[8] found in muscles , tendons ,cartilage , intestine and blood retain mechanical strength and shape . Hydrogels reinforced with fibers improves the mechanical performance.

Polymerization or copolymerization of a variety of monomers with minor amount of crosslinking agents may synthesize hydrogels. Ionic hydrogels are prepared combining neutral or ionic monomers or by partial hydrolysis of gel after synthesis[9-12] . Such gels behave in cyclic manner in solution of different pH . Neutral gels based on water- soluble polymers or copolymer backbones have been prepared and these show LCST phenomenon .If hydrogel is composed of lightly crosslinked matrix then gel will shrink significantly over a narrow temperature range . Thermosensitive gels loose absorbed water at and above LCST [13] and become stiff [14,15].
This phenomenon is reversed when hydrogel is cooled below LCST where gel returns to swollen and soft state . Varieties of methods are known for change of LCST , rate of shrinking and swelling and permeation rate of substances in gels . These techniques include , copolymerising monomer exhibiting LCST with more hydrophilic or hydrophobic monomers[16-18] , variation of crosslinking density[19,20] or change of the ionic strength of solution[21,22].Since swelling and shrinking occurs over a low temperature range hence earlier absorbed substances can be released or delivered at specific temperatures .

In general, highly swollen hydrogels include those of cellulose derivatives, poly(vinyl alcohol), poly(*N*-vinyl-2-pyrrolidone) (PNVP), and poly(ethylene glycol), among others. Moderately and poorly swollen hydrogels are those of poly(hydroxyethyl methacrylate) (PHEMA) and many of its derivatives.
In general, a basic hydrophilic monomer can be copolymerized with other more or less hydrophilic monomers to achieve desired swelling properties. Such processes have led to a wide range of swellable hydrogels, as Gregonis *et al*. (1976), Peppas (1987, 1997), and others have pointed out.

Knowledge of the swelling characteristics of a polymer is of utmost importance in biomedical and pharmaceutical applications since the equilibrium degree of swelling influences (i) the solute diffusion coefficient through these hydrogels, (ii) the surface properties and surface mobility, (iii) the optical properties, especially in relation to contact lens applications, and (iv) the mechanical properties.

4.2. **Factors affecting swelling behaviour of hydrogels**

Swelling behaviour of hydrogels is mainly affected by the structural and environmental factors as discussed briefly .At equilibrium swelling there is a balance between cohesive and dispersive forces . Factors those affect swelling behaviour are given below [23]

4.2.1.Structural factors affecting swelling:

These are also termed as internal factors and these factors can be tailored by synthetic conditions that determine swellability of hydrogels. A hydrogel of desired swellability can be designed by proper combination of monomers Crosslinking of hydrophilic and hydrophobic moieties and change of monomer concentration results in the formation of hydrogel of varying swellability.

A porous structure accelerate the extent of swelling [24-26] . De Boer et al[27]. have reported that solution crosslinked polyethylene could swell to higher limit than bulk crosslinked samples. It has been observed that modification of poly(N-i-PAAm) gel with biomer via semi-interpenetrating network formation did not affect the gel collapse point but decreases extent of swelling and thermo sensitivity .

Factors increase swelling	**Factors decrease swelling**
Dispersive forces	Cohesive forces
Hydrophilic group and moieties	Hydrophobic group and moieties
Low crosslinking density	High crosslinking density
High chain flexibility	Low chain flexibility
High free energy volume	Low free energy volume
Dipole- Dipole interactions	Osmotic potential
Impurities in fluid	Electrostatic repulsion

4.2.2.Environmental factors affecting swelling[24a]

Dynamics of swelling is greatly affected by factors given in the table below

Physical	Chemical
Temperature	pH
Ionic strength	Specific ions
Solvents	Chemical agents
Radiation (UV, visible)	
Electric fields	Biochemical
Mechanical stress	Enzyme substrates
High pressure	Affinity ligands
Sonic radiation	Other biological agents
Magnetic fields	

It has been reported that in a mixture of o-toluedene - water , hydrolysed Starch-g-poly(acrylonitrile) gel absorbs 30% of water within 10 minutes .Hydrogel swelling as a function of temperature has been widely exploited by the workers in recent years . Decrease in swelling levels ,i.e., negative thermo sensitivity , is observed in gels obtained by crosslinking of polymer those exhibits LCST in aqueous

situation .LCST results from influence of temperature on polymer-polymer and polymer- water interactions such as hydrogen bonding and hydrophobic interactions. LCST is shown by hydrophobic , water soluble non- ionic polymers poly(N-i-PAAm).Some other examples are N-n-propyl acrylamide and N-cyclopropyl acrylamide Swelling of these hydrogels is greatly affected by anionic surfactants . These surfactants convert non-ionic gel in to polyelectrolyte gel through binding of surfactants [28] and it causes change in transition temperature [29].Polyeletrolyte hydrogels present in contact with solution of electrolyte sorb some ions preferentially leaving others in solutions[30] .This behaviour reveals that counter ion- poly ion interaction is most essential factor governing functions of polyelectrolyte hydrogels . Hydrogel contract in presence of electric field[31,32] .First part of this chapter deals with swelling study of hydrogels prepared in chapter 2 as a function of time temperature and pH of medium to determine potential end use of hydrogels.

4.3.1. THEORY OF SWELLING BEHAVIOR[.24a]

The physical behavior of hydrogels is dependent on their equilibrium and dynamic swelling behavior in water, since upon preparation they must be brought in contact with water to yield the final, swollen network structure. Figure given below shows one of two possible processes of swelling. A dry, hydrophilic crosslinked network is placed in water. Then, the macromolecular chains interact with the solvent molecules owing to the relatively good thermodynamic compatibility. Thus, the network expands to the solvated state.

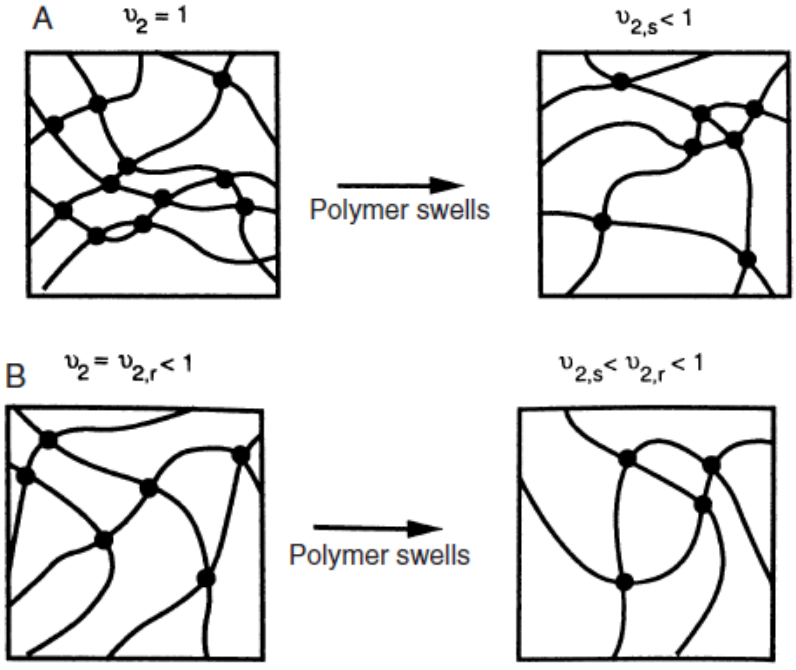


Fig: (A) Swelling of a network prepared by cross-linking in dry state. (B) Swelling of a network prepared by cross-linking in solution.

The Flory-Huggins theory can be used to calculate thermodynamic quantities related to that mixing process. Flory (1953) developed the initial theory of the swelling of cross-linked polymer gels using a Gaussian distribution of the polymer chains.

His model describing the equilibrium degree of cross-linked polymers postulated that the degree to which a polymer network swelled was governed by the elastic retractive forces of the polymer chains and the thermodynamic compatibility of the polymer and the solvent molecules. In terms of the free energy of the system, the total free energy change upon swelling was written as:

$$\Delta G = \Delta G_{\text{elastic}} + \Delta G_{\text{mix}} \qquad (1)$$

Here, $\Delta G_{\text{elastic}}$ is the contribution due to the elastic retractive forces and ΔG_{mix} represents the thermodynamic compatibility of the polymer and the swelling agent (water). Upon differentiation of Eq. 1 with respect to the water molecules in the system, an expression can be derived for the chemical potential change of water in terms of the elastic and mixing contributions due to swelling.

$$\mu_1 - \mu_{1,0} = \Delta\mu_{\text{elastic}} + \Delta\mu_{\text{mix}} \qquad (2)$$

Here, $\mu 1$ is the chemical potential of water within the gel and $\mu 1,0$ is the chemical potential of pure water. At equilibrium, the chemical potentials of water inside and outside of the gel must be equal. Therefore, the elastic and mixing contributions to the chemical potential will balance one another at equilibrium. The chemical potential change upon mixing can be determined from the heat of mixing and the entropy of mixing.

Using the Flory–Huggins theory, the chemical potential of mixing can be expressed as:

$$\Delta\mu_{\text{mix}} = RT\left(\ln(1 - 2\upsilon_{2,s}) + \upsilon_{2,s} + \chi_1\upsilon_{2,s}^2\right) \qquad (3)$$

where $\chi 1$ is the polymer-water interaction parameter, $\upsilon 2,s$ is the polymer volume fraction of the gel, T is absolute temperature, and R is the gas constant.

This thermodynamic swelling contribution is counterbalanced by the retractive elastic contribution of the cross-linked structure. The latter is usually described by the rubber elasticity theory and its variations (Peppas, 1987). Equilibrium is attained in a particular solvent at a particular temperature when the two forces become equal.

The volume degree of swelling, Q (i.e., the ratio of the actual volume of a sample in the swollen state divided by its volume in the dry state), can then be determined from Eq. 4.

$$\upsilon_{2,s} = \frac{\text{Volume of polymer}}{\text{Volume of swollen gel}} = \frac{V_p}{V_{\text{gel}}} = 1/Q \qquad (4)$$

Researchers working with hydrogels for biomedical application prefer to use other parameters in order to define the equilibrium-swelling behavior. For example, Yasuda *et al.* (1969) introduced the use of the so-called hydration ratio, *H*, which has been accepted by those researchers who use hydrogels for contact lens applications (Peppas and Yang, 1981). Another definition is that of the weight degree of swelling, *q*, which is the ratio of the weight of the swollen sample to that of the dry sample.

4.3.2.Rubber Elasticity Theory

The other theory used to determine crosslinked structure of a gel is the rubber elasticity theory. Hydrogels resemble natural rubbers in their property to elastically respond to applied stress. Thus when a crosslinked network is stretched, it reaches an equilibrium strain while the stress remains constant. A hydrogel subjected to small deformation, less than 20% [(33)] will fully recover to its original dimension rapidly. The rubber elasticity theory [(34)] is used to explain this behavior, thermodynamically. This theory was first developed by Treolar [(35)] and Flory [(34)] for vulcanized rubbers and modified to polymers. Later expressions were developed which apply to hydrogels prepared in presence of solvent [(36)] .

According to the modified theory for hydrogels prepared in presence of solvent, we have

$$\tau = \frac{\rho RT}{\bar{M}_c}\left(1 - \frac{2\bar{M}_c}{\bar{M}_n}\right)\left(\alpha - \frac{1}{\alpha^2}\right)\left(\frac{v_{2,s}}{v_{2,r}}\right)^{\frac{1}{3}}$$

Here τ is the stress applied to the polymer sample, ρ is the density of the polymer, R is the universal gas constant, T is the absolute experimental temperature, and Mc the average molecular weight between crosslinks.

To be able to analyse the structure of the hydrogel using this theory, experiments need to be performed using a tensile system. This theory can be used to analyse chemically, physically crosslinked as well as hydrogels exhibiting temporary crosslinks due to hydrogen bonding.

4.4.EXPERIMENTAL:

Swelling behaviour of all hydrogels prepared in chapter 2 was studied in aqueous media.

4.4.1.Measurement of the % of Swelling as a function of time

For the swelling studies, the dried samples were placed in distilled water at Room temperature (approx. 20^0 in the month of February 2011) and removed from water at regular time intervals(1,2,3,4,5,6,7,8 and 24 hours). After the water on the surfaces of the hydrogels was wiped off with moistened filter paper, the weights of the hydrogels were recorded. The swelling (%) was calculated as follows;

$$Ps = \frac{Ws - Wd}{Wd} \times 100$$

4.4.2.Measurement of the % of Swelling as a function of *p*H:

Samples were dipped in water having different pH (5,6,7,8,9) for 2 hours then removed and wiped off with moistened filter paper, the weights of the hydrogels were recorded. The swelling (%) was calculated as above in the case of time.

4.4.3.Measurement of the % of Swelling as a function of temp:

Samples were dipped in water at temperature (RT, 27,32,37,and 42^0C) for 2 hours then removed and wiped off with moistened filter paper, the weights of the hydrogels were recorded. The swelling (%) was calculated as above in the case of time.

4.5.Result and Discussions:

Swelling behaviour of various hydrogels has been explained on the basis of various theories modelled, especially, to study volume transitions in hydrogels. Volume transition has been attributed to hydrophobic interactions [(37)]. Compressible lattice theory has been used to predict transitions by defining interaction parameters on the basis of large differences in cohesive energy densities of components [(38,39)]. External lattice fluid hydrogen bond theory to model swelling behaviour of PEO and poly(N-i-PAAm) hydrogels was proposed by Lele et al[(40)]. It was suggested by hydrogen bonding interactions as well as hydrophobic interactions are crucial for volume transitions. Further dissolution of network chains in the solvent is prevented by crosslinks of temporary or of permanent nature. Equilibrium swelling is achieved by balance of osmotic forces of mixing and elastic forces of network. Prange et al[(41)]have suggested that every segment of the molecule have three types of contact sites : proton donating, proton accepting and those , which interact through dispersion forces. Swelling behaviour pattern of various polymeric hydrogels as a function of time, pH and temperature has been discussed below.

4.5.1.Swelling as a function of time:

4.5.1.1.Swelling of hydrogel 1 vs time

For hydrogel 1; % of swelling for 8 hours is 258% and for next 16 hours i.e., at 24 hours % of swelling is 352%; also for 1^{st} hour it is 100 %. Thus we can say that % of swelling with time is not linear but it is between linear and exponential curves. It is clear that extent of swelling increases with time but swelling rate decreases with time;

perhaps it is due to the fact that as time goes on there is decrease in number of holes /pores present in network. Also there competition between swelling and deswelling ; as we know that as extent of water in polymer network increases there must increase in deswelling rate; thus resultant swelling rate must decrease and it obtained in graph 1.

4.5.1.2.Swelling of hydrogel 2 vs time:

For hydrogel 2; % of swelling for 8 hours is 152% and for next 16 hours i.e., at 24 hours % of swelling is 231%; also for 1st hour it is 50 %. Thus we can say that % of swelling with time is not linear but it is between linear and exponential curves. It is clear that extent of swelling increases with time but swelling rate decreases with time; perhaps it is due to the fact that as time goes on there is decrease in number of holes /pores present in network. Also there competition between swelling and deswelling ; as we know that as extent of water in polymer network increases there must increase in deswelling rate; thus resultant swelling rate must decrease and it obtained in graph 2. It is also seen that extent of swelling for same time in the case of hydrogel 2 is lesser than that in case of 1 because there is more degree of crosslinking in case of 2 due presence of more polar groups present for crosslinking; –COOH and -$CONH_2$ both are present in hydrogel 2.

4.5.1.3.Swelling of hydrogel 3 vs time:

For hydrogel 3; % of swelling for 8 hours is 85 % and for next 16 hours i.e., at 24 hours % of swelling is 125 %; also for 1st hour it is 20 %. Thus we can say that % of swelling with time is not linear but it is between linear and exponential curves. It is clear that extent of swelling increases with time but swelling rate decreases with time; perhaps it is due to the fact that as time goes on there is decrease in number of vacant holes /pores present in network. Also there competition between swelling and deswelling ; as we know that as extent of water in polymer network increases there must increase in deswelling rate; thus resultant swelling rate must decrease and it obtained in graph 3. It is also seen that extent of swelling for same time in the case of hydrogel 3 is lesser than that in case of 1 because there is more degree of crosslinking in case of 3 due presence of more polar groups present for crosslinking; –COOH and -$CONH_2$ both are present in hydrogel 3.

4.5.1.4.Swelling of hydrogel 4 vs time:

For hydrogel 4; % of swelling for 8 hours is 295 % and for next 16 hours i.e., at 24 hours % of swelling is 373 %; also for 1st hour it is 100 %. Thus we can say that % of swelling with time is not linear but it is between linear and exponential curves. It is clear that extent of swelling increases with time but swelling rate decreases with time; perhaps it is due to the fact that as time goes on there is decrease in number of vacant holes /pores present in network. Also there competition between swelling and deswelling ; as we know that as extent of water in polymer network increases there must increase in deswelling rate; thus resultant swelling rate must decrease and it is obtained in graph 4. It is also seen that extent of swelling for same time in the case of hydrogel 4 is higher than that in case of 1 because there is lower degree of

crosslinking in case of 4 due presence of lesser polar groups present for crosslinking; (–OH with -$CONH_2$) and due to bulky nature of sugar.

4.5.1.5.Swelling of hydrogel 5 vs time:

For hydrogel 5; % of swelling for 8 hours is 380 % and for next 16 hours i.e., at 24 hours % of swelling is 578 %; also for 1st hour it is 101 %. Thus we can say that % of swelling with time is not linear but it is between linear and exponential curves. It is clear that extent of swelling increases with time but swelling rate decreases with time; perhaps it is due to the fact that as time goes on there is decrease in number of vacant holes /pores present in network. Also there competition between swelling and deswelling ; as we know that as extent of water in polymer network increases there must increase in deswelling rate; thus resultant swelling rate must decrease and it is obtained in graph 5. It is also seen that extent of swelling for same time in the case of hydrogel 5 is higher than that in case of 1 because there is lower degree of crosslinking in case of 5 due presence of lesser polar groups present for crosslinking; (–OH with -$CONH_2$,- COOH, polypeptides). Pores are also more due to bulky nature of chemicals present in pineapple like protiens, sugars , lipids and fats etc.

4.5.1.6.Swelling of hydrogel 6 vs time:

For hydrogel 6; % of swelling for 8 hours is 367 % and for next 16 hours i.e., at 24 hours % of swelling is 527 %; also for 1st hour it is 87 %. Thus we can say that % of swelling with time is not linear but it is between linear and exponential curves. It is clear that extent of swelling increases with time but swelling rate decreases with time; perhaps it is due to the fact that as time goes on there is decrease in number of vacant holes /pores present in network. Also there competition between swelling and deswelling ; as we know that as extent of water in polymer network increases there must increase in deswelling rate; thus resultant swelling rate must decrease and it is obtained in graph 6. It is also seen that extent of swelling for same time in the case of hydrogel 6 is higher than that in case of 1 because there is lower degree of crosslinking in case of 6 due presence of lesser polar groups present for crosslinking; (–OH with -$CONH_2$,- COOH, polypeptides). Pores are also more due to bulky nature of chemicals present in pineapple like protiens, sugars , lipids and fats etc.

4.5.1.7.Swelling of hydrogels vs time:

From combined graph 7; it is clear that due more crosslinking in the case of hydrogel 2 and hydrogel 3; extent of swelling is lower while in case of hydrogels from natural resources; extent of swelling is higher due lower degree of crosslinking.
Thus regarding swelling behaviour; hydrogels from natural resources are superior than that of polyacrylamide hydrogels. Hydrogel from Sapodilla (Manilkara Zapota) is best regarding swelling and hydrogel from Acrylamide co polymerised with Methacrylicacid is worst regarding swelling.

4.5.2.Swelling of hydrogel vs pH:

4.5.2.1. Swelling of hydrogel 1 vs pH:

From graph 8; it is clear that for pH range (5-9) ; %S is maximum at pH 5 and decreases as pH increases and gets minimum value at pH 7 and again increases in alkaline media and gets another maxima at pH 9. In polyacrylamide hydrogel; there is only amide functional group. At lower pH amide are protonated to some extent so there will be repulsion between $–NH_3^+$ and$–NH_3^+$ due to this electrostatic repulsion ; % S is maximum and %S decreases with pH and at pH 7 as no amide group is protonated hence there will be hydrogen bonding between -CO and- NH_2 of different amide groups hence %S is minimum. As pH increases there is conversion of amide group to carboxylate group[42] so again electrostatic repulsion increases hence %S increases .

4.5.2.2..Swelling of hydrogel 2 vs pH:

From graph 9; it is clear that for pH range (5-9); %S is maximum at pH 5 and decreases as pH increases and gets minimum value at pH 7 and again increases in alkaline media and gets another maxima at pH 9. In hydrogel 2 there are two functional groups $–CONH_2$ and –COOH; at lower pH acid group is in unionised form while amide is in protonated form there will be repulsion between protonated groups and no chance of hydrogen bonding in acid and protonated amide group so %S is higher . At pH 7 both amide as well as acid are in unionised form so there is hydrogen bonding hence %S is least. When alkalinity increases again there is ionised $–COO^-$ group is present hence electrostatic repulsion exists and high %S.

4.5.2.3..Swelling of hydrogel 3 vs pH:

From graph 10; it is clear that for pH range (5-9); %S is maximum at pH 5 and decreases as pH increases and gets minimum value at pH 7 and again increases in alkaline media and gets another maxima at pH 9. In hydrogel 3 there are two functional groups $–CONH_2$ and –COOH; at lower pH acid group is in unionised form while amide is in protonated form there will be repulsion between protonated groups and no chance of hydrogen bonding in acid and protonated amide group so %S is higher . At pH 7 both amide as well as acid are in unionised form so there is hydrogen bonding hence %S is least. When alkalinity increases again there is ionised $–COO^-$ group is present hence electrostatic repulsion exists and high %S.

4.5.2.4.Swelling of hydrogel 4 vs pH:

From graph 11; it is clear that for pH range (5-9); %S is maximum at pH 5 and decreases as pH increases and gets minimum value at pH 7 and again increases in alkaline media and gets another maxima at pH 9. In hydrogel 4 there are two functional groups $–CONH_2$ and –OH; at lower pH alcohol as well as amide is in protonated form there will be repulsion between protonated groups and no chance of hydrogen bonding so %S is higher . At pH 7 both amide as well as hydroxyl groups are in unionised form so there is hydrogen bonding hence %S is least. When alkalinity

increases again there is ionised –COO^- group is present with -OH hence electrostatic repulsion exists and lesser chance of hydrogel bonding and hence high %S.

4.5.2.5.Swelling of hydrogel 5 vs pH:

From graph 12; it is clear that for pH range (5-9); %S is maximum at pH 5 and decreases as pH increases and gets minimum value at pH 7 and again increases in alkaline media and gets another maxima at pH 9. In hydrogel 5 functional groups are –$CONH_2$ -COOH and –OH; at lower pH alcohol as well as amide is in protonated form and –COOH is unionised so there will be repulsion between protonated groups and no chance of hydrogen bonding so %S is higher . At pH 7; all functional groups are in unionised form so there is hydrogen bonding hence %S is least. When alkalinity increases again there is ionised –COO^- group is present with -OH hence electrostatic repulsion exists and lesser chance of hydrogel bonding and hence high %S.

4.5.2.6.Swelling of hydrogel 6 vs pH:

From graph 13; it is clear that for pH range (5-9); %S is maximum at pH 5 and decreases as pH increases and gets minimum value at pH 7 and again increases in alkaline media and gets another maxima at pH 9. In hydrogel 6 functional groups are –$CONH_2$ -COOH and –OH; at lower pH alcohol as well as amide is in protonated form and –COOH is unionised so there will be repulsion between protonated groups and no chance of hydrogen bonding so %S is higher . At pH 7; all functional groups are in unionised form so there is hydrogen bonding hence %S is least. When alkalinity increases again there is ionised –COO^- group is present with -OH hence electrostatic repulsion exists and lesser chance of hydrogel bonding and hence high %S.

4.5.2.7.Swelling of hydrogels vs pH:

From graph 14; it is obvious that hydrogel based on natural resources are more pH responsive than that of copolymerised with carboxylic acid .It is due to the fact that there is more crosslinking and hydrogen bonding in case of later case .

4.5.3.Swelling of hydrogel vs temp:

4.5.3.1.Swelling of hydrogel 1 vs temp:

From graph 15; it is clear that extent of swelling increases with temperature ; it may be due to thermal expansion of crosslinks . At Room Temperature; % S is 107% but at 42^0C; % S is 471% .Thus between Room temperature and 42^0C there regular increase in % of swelling with temperature but it will decrease after a certain temperature.

4.5.3.2.Swelling of hydrogel 2 vs temp:

From graph 16; it is clear that extent of swelling increases with temperature; it may be due to thermal expansion of crosslinks . At Room Temperature; % S is 48% but at 32^0C; % S is 98% .Thus between Room temperature and 32^0C there regular increase in % of swelling with temperature but it is nearly constant after this because at 42^0C

%S is 103%. Lower % of swelling at same temp for hydrogel 2 than 1 is explained as in explanation 2.

4.5.3.3.Swelling of hydrogel 3 vs temp:

From graph 17; it is clear that extent of swelling increases with temperature; it may be due to thermal expansion of crosslinks. At Room Temperature; % S is 16% but at 42^0C; % S is 87% .Thus between Room temperature and 42^0C there regular increase in % of swelling with temperature. Lower % of swelling at same temp for hydrogel 3 than 1 is explained as in explanation 3.

4.5.3.4.Swelling of hydrogel 4 vs temp:

From graph 18; it is clear that extent of swelling increases with temperature; it may be due to thermal expansion of crosslinks. At Room Temperature; % S is 146% but at 42^0C ; % S is 253% .Thus between Room temperature and 42^0C there regular increase in % of swelling with temperature but it will decrease after a certain temperature .At room temperature %S for hydrogel 4 is more than 1 ; it can be explained as in explanation 4.

4.5.3.5.Swelling of hydrogel 5 vs temp:

From graph 19; it is clear that extent of swelling increases with temperature; it may be due to thermal expansion of crosslinks. At Room Temperature; % S is 159% but at 42^0C; % S is 214% .Thus between Room temperature and 42^0C there regular increase in % of swelling with temperature but it will decrease after a certain temperature. At room temperature %S for hydrogel 5 is more than 1; it can be explained as in explanation 5.

4.5.3.6.Swelling of hydrogel 6 vs temp:

From graph 20; it is clear that extent of swelling increases with temperature; it may be due to thermal expansion of crosslinks. At Room Temperature; % S is 125% but at 42^0C; % S is 408% .Thus between Room temperature and 42^0C there regular increase in % of swelling with temperature but it will decrease after a certain temperature. At room temperature %S for hydrogel 6 is more than 1; it can be explained as in explanation 6.

4.5.3.7.Swelling of hydrogels vs temp:

From graph 21; it is evident that for all hydrogels; there is an increase in %S as temperature increases. For hydrogel 2 and hydrogel3 there is lower %S due high crosslinking and for hydrogel based on natural resources initially at room temperature %S is higher than that for hydrogel 1 due low crosslinking but as temperature rises more increase in pore size for hydrogel 1 is observed in comparision to hydrogel based on natural resources.

SWELLING RESULTS OF HYDROGELS IN TABULER FORM

TABLE 1

SWELLING OF HYDROGEL 1 vs TIME

S.N	TIME (HOURS)	Wd (gm)	Ws (gm)	W (gm)	%S
1	0	0.634	0.634	0	0
2	1	0.634	1.268	0.634	100
3	2	0.634	1.585	0.951	150
4	3	0.634	1.806	1.172	185
5	4	0.634	1.933	1.299	205
6	5	0.634	2.022	1.388	219
7	6	0.634	2.161	1.527	241
8	7	0.634	2.219	1.585	250
9	8	0.634	2.269	1.635	258
10	24	0.634	2.865	2.231	352

TABLE 2

SWELLING OF HYDROGEL 2 vs TIME

S.N	TIME (HOURS)	Wd (gm)	Ws (gm)	W (gm)	%S
1	0	1.511	1.511	0	0
2	1	1.511	2.266	0.755	50
3	2	1.511	2.719	1.208	80
4	3	1.511	3.052	1.541	102
5	4	1.511	3.278	1.767	117
6	5	1.511	3.445	1.934	128
7	6	1.511	3.581	2.07	137
8	7	1.511	3.701	2.19	145
9	8	1.511	3.807	2.296	152
10	24	1.511	5.001	3.49	231

TABLE 3

SWELLING OF HYDROGEL 3 vs TIME

S.N	TIME (HOURS)	Wd (gm)	Ws (gm)	W (gm)	%S
1	0	0.665	0.665	0	0
2	1	0.665	0.798	0.133	20
3	2	0.665	0.897	0.232	35
4	3	0.665	0.977	0.312	47
5	4	0.665	1.05	0.385	58
6	5	0.665	1.11	0.445	67
7	6	0.665	1.157	0.492	74
8	7	0.665	1.197	0.532	80
9	8	0.665	1.23	0.565	85
10	24	0.665	1.496	0.831	125

TABLE 4

SWELLING OF HYDROGEL 4vs TIME

S.N	TIME (HOURS)	Wd (gm)	Ws (gm)	W (gm)	%S
1	0	0.34	0.34	0	0
2	1	0.34	0.68	0.34	100
3	2	0.34	0.836	0.496	146
4	3	0.34	0.965	0.625	184
5	4	0.34	1.074	0.734	216
6	5	0.34	1.166	0.826	243
7	6	0.34	1.237	0.897	264
8	7	0.34	1.295	0.955	281
9	8	0.34	1.343	1.003	295
10	24	0.34	1.608	1.268	373

TABLE 5

SWELLING OF HYDROGEL 5 vs TIME

S.N	TIME (HOURS)	Wd (gm)	Ws (gm)	W (gm)	%S
1	0	0.433	0.433	0	0
2	1	0.433	0.87	0.437	101
3	2	0.433	1.121	0.688	159
4	3	0.433	1.337	0.9	209
5	4	0.433	1.524	1.087	252
6	5	0.433	1.684	1.247	289
7	6	0.433	1.827	1.39	322
8	7	0.433	1.957	1.52	352
9	8	0.433	2.078	1.641	380
10	24	0.433	2.935	2.498	578

TABLE 6

SWELLING OF HYDROGEL 6 vs TIME

S.N	TIME (HOURS)	Wd (gm)	Ws (gm)	W (gm)	%S
1	0	0.394	0.394	0	0
2	1	0.394	0.736	0.342	87
3	2	0.394	0.973	0.579	147
4	3	0.394	1.15	0.756	192
5	4	0.394	1.327	0.933	237
6	5	0.394	1.481	1.087	276
7	6	0.394	1.615	1.221	310
8	7	0.394	1.733	1.339	340
9	8	0.394	1.839	1.445	367
10	24	0.394	2.47	2.076	527

TABLE 7

SWELLING OF HYDROGELS vs TIME

S.N	TIME (HOURS)	%S1	%S2	%S3	%S4	%S5	%S6
1	0	0	0	0	0	0	0
2	1	100	50	20	100	101	87
3	2	150	80	35	146	159	147
4	3	185	102	47	184	209	192
5	4	205	117	58	216	252	237
6	5	219	128	67	243	289	276
7	6	241	137	74	264	322	310
8	7	250	145	80	281	352	340
9	8	258	152	85	295	380	367
10	24	352	231	125	373	578	527

TABLE 8

SWELLING OF HYDROGEL 1 vs pH

S.N	pH	Wd	Ws	W	% S
1	5	0.065	0.325	0.26	400
2	6	0.048	0.204	0.156	325
3	7	0.063	0.131	0.068	107
4	8	0.092	0.412	0.32	348
5	9	0.084	0.382	0.298	355

TABLE 9

SWELLING OF HYDROGEL 2 vs pH

S.N	pH	Wd	Ws	W	% S
1	5	0.301	0.583	0.282	94
2	6	0.257	0.496	0.239	93
3	7	1.511	2.23	0.719	48
4	8	0.137	0.215	0.078	57
5	9	0.164	0.294	0.13	79

TABLE 10
SWELLING OF HYDROGEL 3 vs pH

S.N	pH	Wd	Ws	W	% S
1	5	0.257	0.376	0.119	47
2	6	0.307	0.451	0.144	47
3	7	0.665	0.774	0.109	16
4	8	0.255	0.385	0.13	51
5	9	0.263	0.432	0.169	64

TABLE 11
SWELLING OF HYDROGEL 4 vs pH

S.N	pH	Wd	Ws	W	% S
1	5	0.111	0.414	0.303	273
2	6	0.14	0.401	0.261	186
3	7	0.34	0.835	0.495	146
4	8	0.176	0.522	0.346	197
5	9	0.158	0.536	0.378	239

TABLE 12
SWELLING OF HYDROGEL 5 vs pH

S.N	pH	Wd	Ws	W	% S
1	5	0.238	0.72	0.482	203
2	6	0.131	0.387	0.256	195
3	7	0.433	1.12	0.687	159
4	8	0.102	0.324	0.222	218
5	9	0.11	0.365	0.255	232

TABLE 13
SWELLING OF HYDROGEL 6 vs pH

S.N	pH	Wd	Ws	W	% S
1	5	0.09	0.366	0.276	307
2	6	0.083	0.312	0.229	276
3	7	0.399	0.886	0.487	125
4	8	0.159	0.469	0.31	192
5	9	0.114	0.386	0.272	239

TABLE 14
SWELLING OF HYDROGELS vs pH

S.N	pH	% S1	% S2	% S3	% S4	% S5	% S6
1	5	400	94	47	273	203	307
2	6	325	93	47	186	195	276
3	7	107	48	16	146	159	125
4	8	348	57	51	197	218	192
5	9	355	79	64	239	232	239

TABLE 15
SWELLING OF HYDROGEL 1 vs Temp (K)

S.N	Temp(K)	Wd	Ws	W	% S
1	RT	0.634	1.31	0.676	107
2	300	0.156	0.63	0.474	304
3	305	0.084	0.426	0.342	407
4	310	0.09	0.465	0.375	417
5	315	0.139	0.794	0.655	471

TABLE 16
SWELLING OF HYDROGEL 2 vs Temp (K)

S.N	Temp(K)	Wd	Ws	W	% S
1	RT	1.511	2.23	0.719	48
2	300	0.467	0.764	0.297	64
3	305	0.222	0.44	0.218	98
4	310	0.188	0.376	0.188	100
5	315	0.214	0.435	0.221	103

TABLE 17
SWELLING OF HYDROGEL 3 vs Temp (K)

S.N	Temp(K)	Wd	Ws	W	% S
1	RT	0.665	0.774	0.109	16
2	300	0.19	0.263	0.073	38
3	305	0.139	0.222	0.083	60
4	310	0.839	1.476	0.637	76
5	315	0.088	0.166	0.078	87

TABLE 18
SWELLING OF HYDROGEL 4 vs Temp (K)

S.N	Temp(K)	Wd	Ws	W	% S
1	RT	0.34	0.835	0.495	146
2	300	0.39	1.09	0.7	179
3	305	0.419	1.254	0.835	199
4	310	0.14	0.453	0.313	224
5	315	0.215	0.76	0.545	253

TABLE 19
SWELLING OF HYDROGEL 5 vs Temp (K)

S.N	Temp(K)	Wd	Ws	W	% S
1	RT	0.433	1.12	0.687	159
2	300	0.216	0.632	0.416	193
3	305	0.15	0.455	0.305	203
4	310	0.13	0.407	0.277	213
5	315	0.255	0.801	0.546	214

TABLE 20
SWELLING OF HYDROGEL 6 vs Temp (K)

S.N	Temp(K)	Wd	Ws	W	% S
1	RT	0.394	0.886	0.492	125
2	300	0.207	0.565	0.358	173
3	305	0.151	0.612	0.461	305
4	310	0.105	0.501	0.396	377
5	315	0.059	0.3	0.241	408

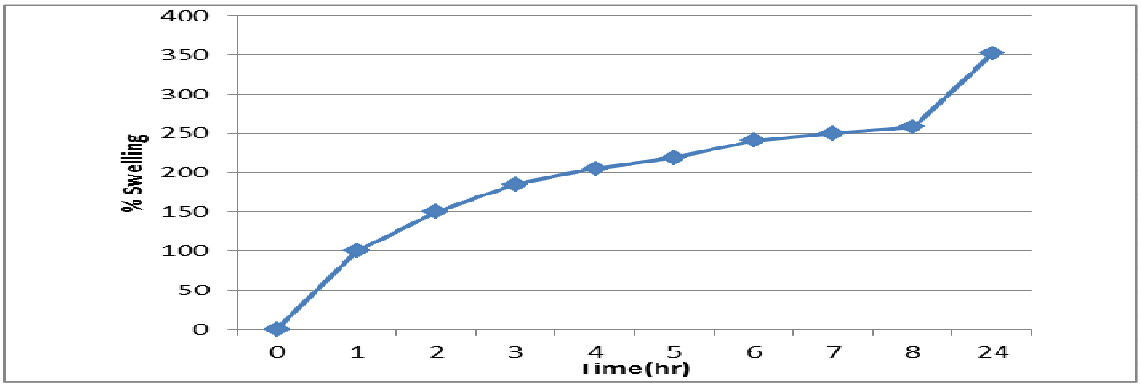
TABLE 21
SWELLING OF HYDROGELS vs Temp (K)

S.N	Temp(K)	% S1	% S2	% S3	% S4	% S5	% S6
1	RT	107	48	16	146	159	125
2	300	304	64	38	179	193	173
3	305	407	98	60	199	203	305
4	310	417	100	76	224	213	377
5	315	471	103	87	253	214	408

SWELLING RESULT OF HYDROGEL IN GRAPHICAL FORM

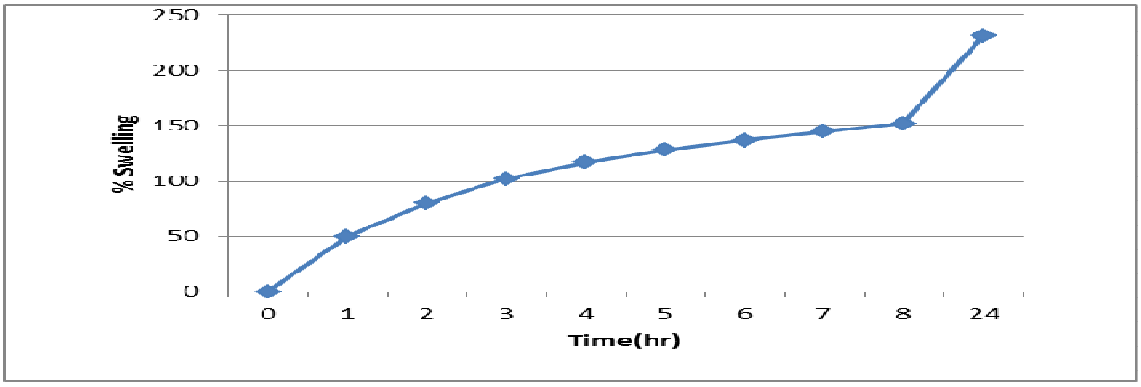
GRAPH 1

SWELLING OF HYDROGEL 1 vs TIME



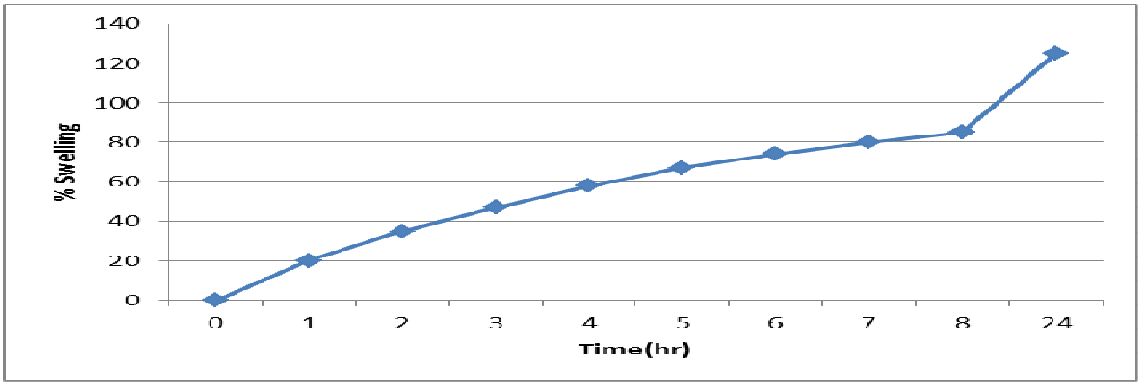
GRAPH 2

SWELLING OF HYDROGEL 2 vs TIME

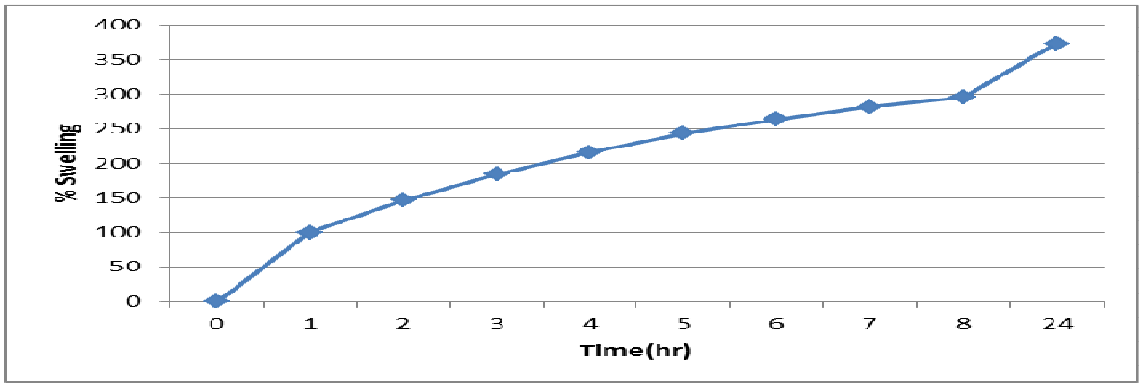


GRAPH 3

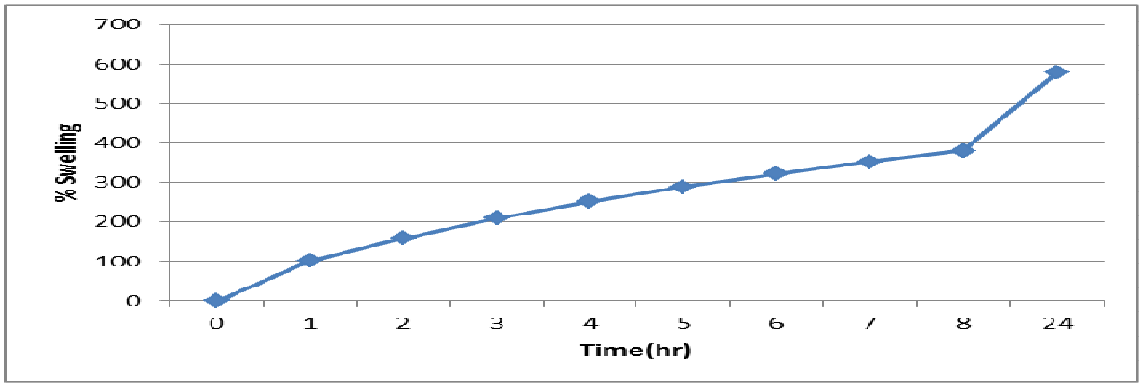
SWELLING OF HYDROGEL 3 vs TIME



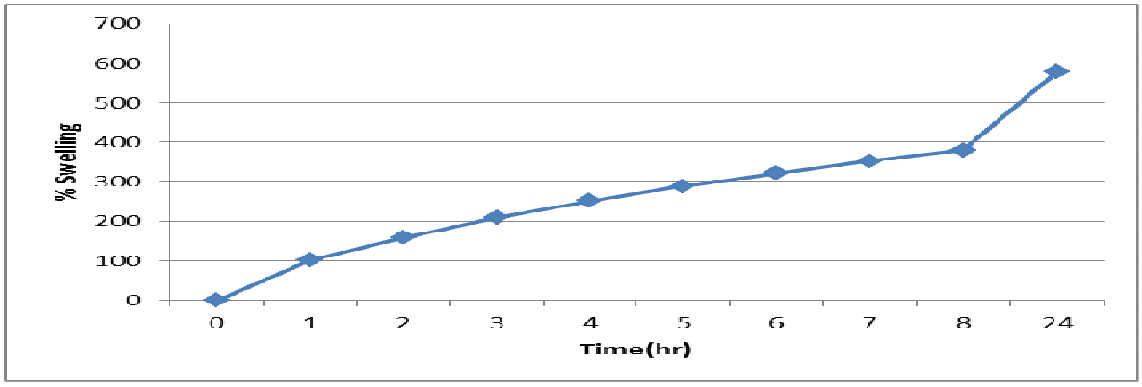
GRAPH 4
SWELLING OF HYDROGEL 4 vs TIME



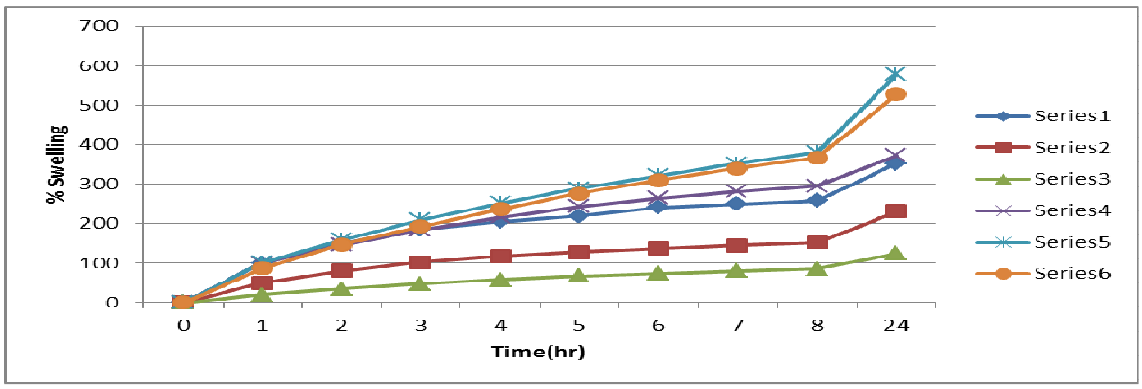
GRAPH 5
SWELLING OF HYDROGEL 5 vs TIME



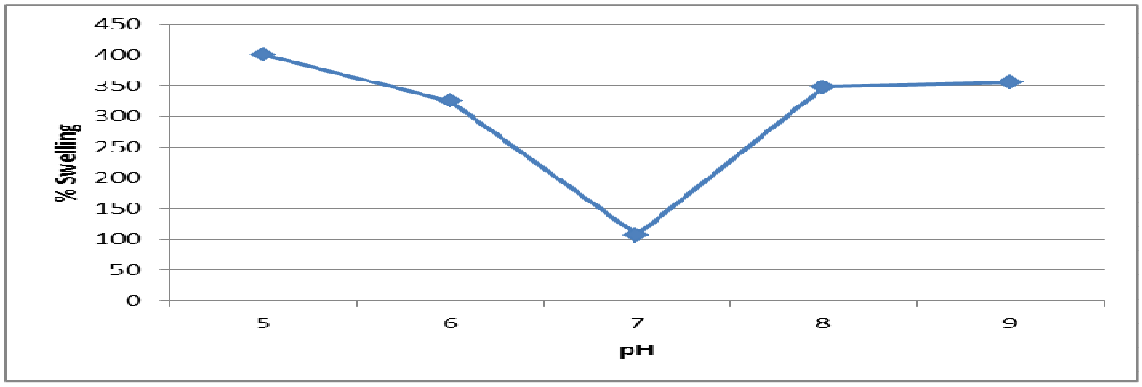
GRAPH 6
SWELLING OF HYDROGEL 6vs TIME



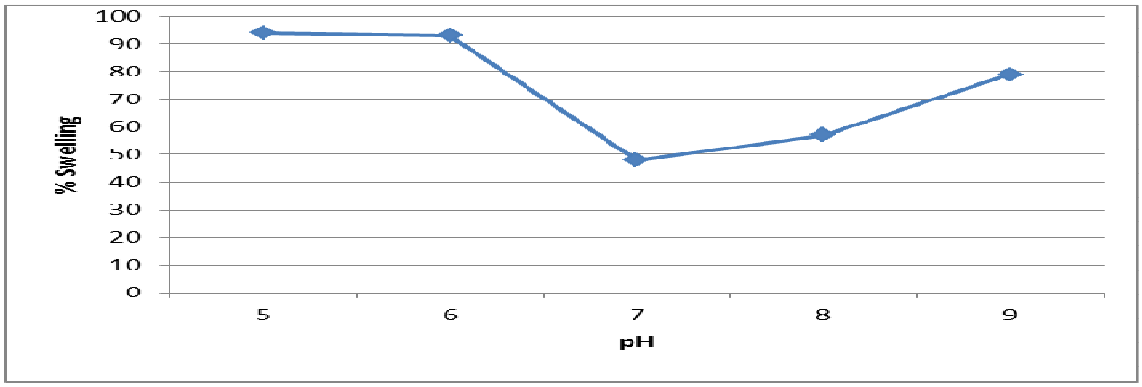
GRAPH 7
SWELLING OF HYDROGELS vs TIME



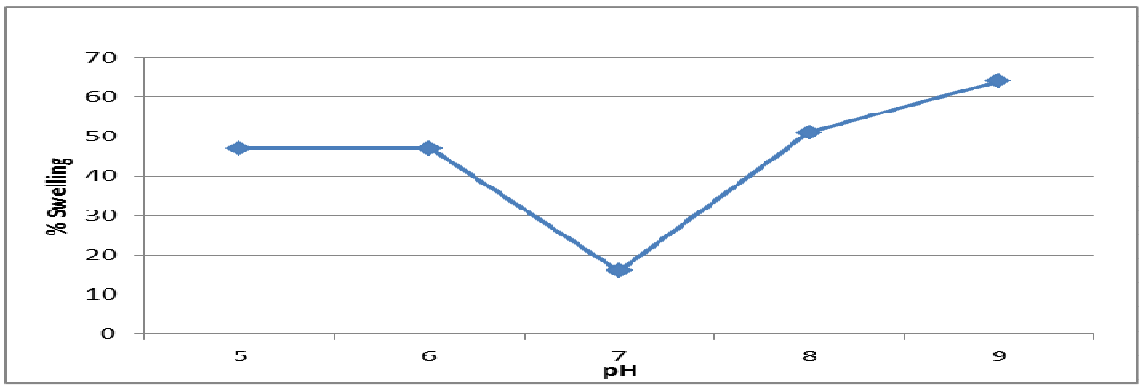
GRAPH 8
SWELLING OF HYDROGEL 1 vs pH



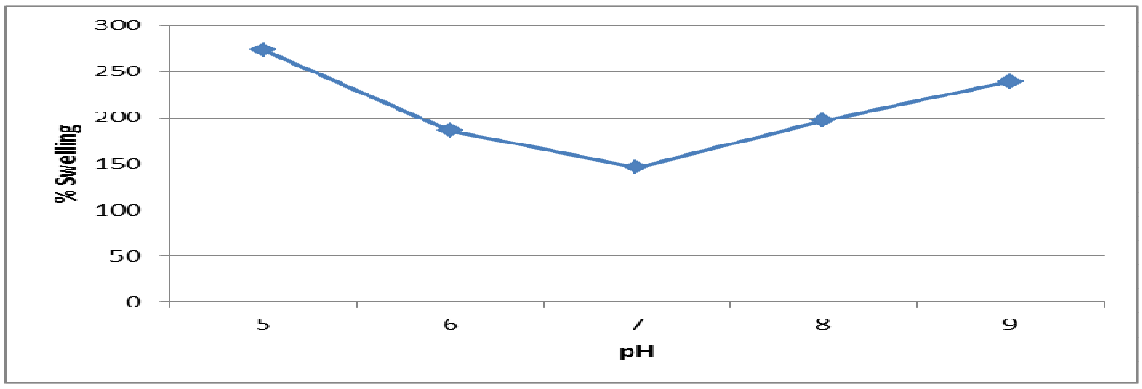
GRAPH 9
SWELLING OF HYDROGEL 2vs pH



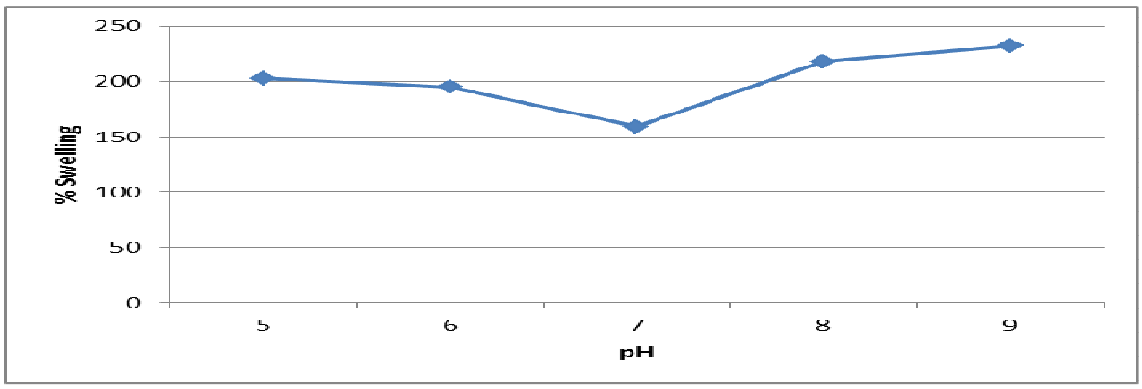
GRAPH 10
SWELLING OF HYDROGEL 3vs pH



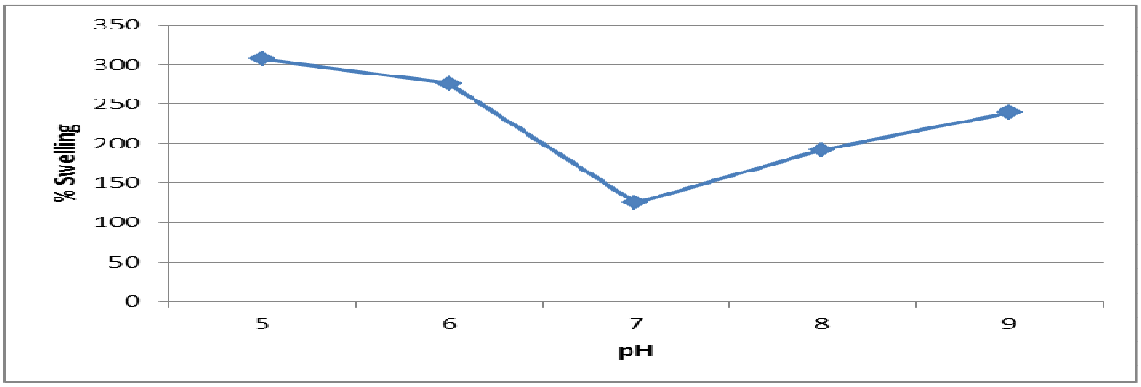
GRAPH 11
SWELLING OF HYDROGEL 4vs pH



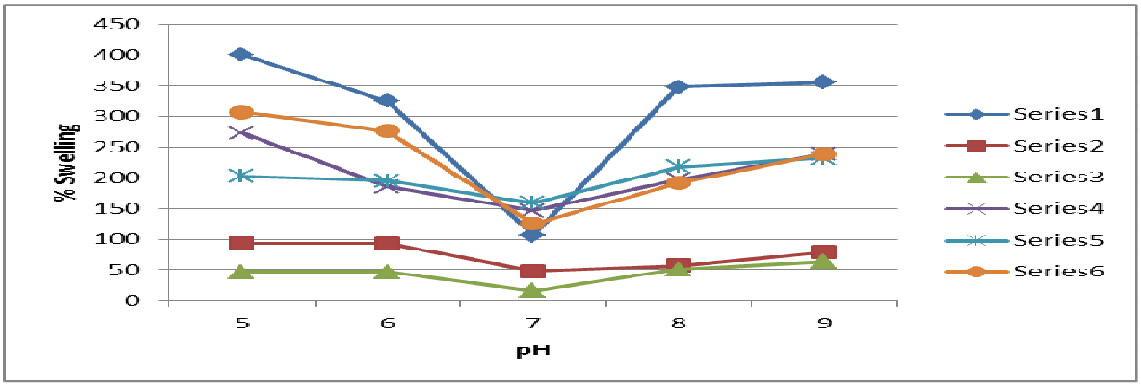
GRAPH 12
SWELLING OF HYDROGEL 5vs pH



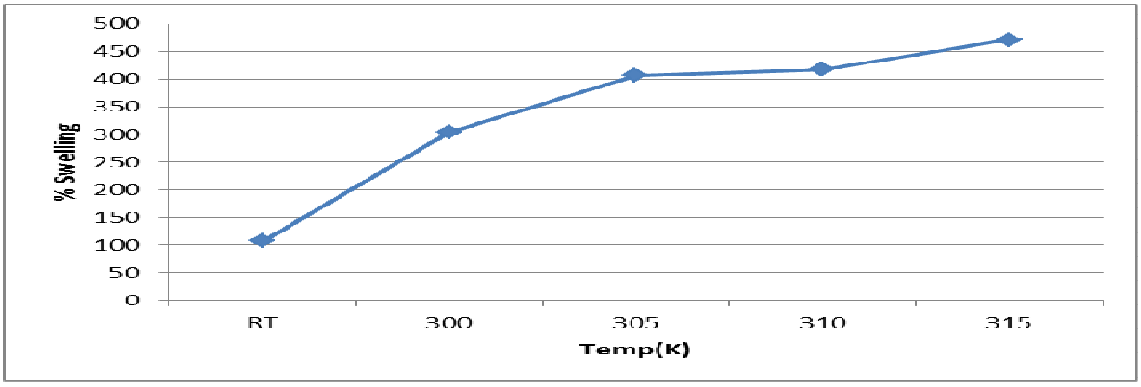
GRAPH 13
SWELLING OF HYDROGEL 6vs pH



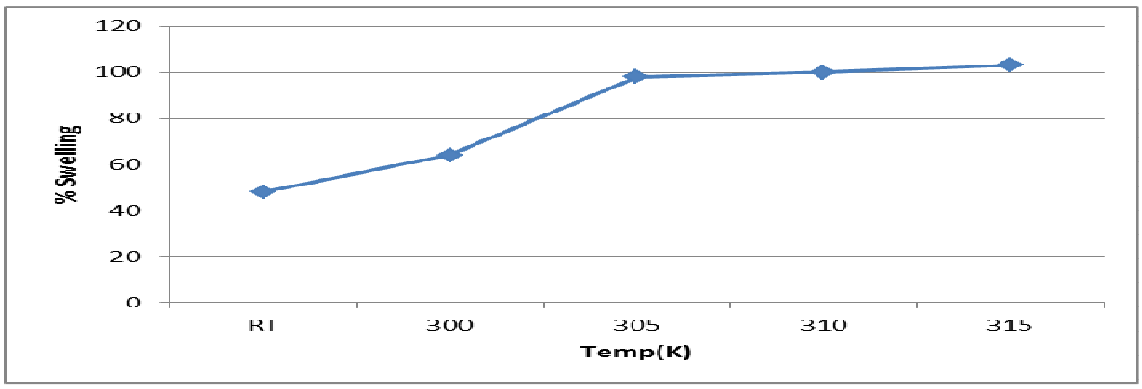
GRAPH 14
SWELLING OF HYDROGELS vs pH



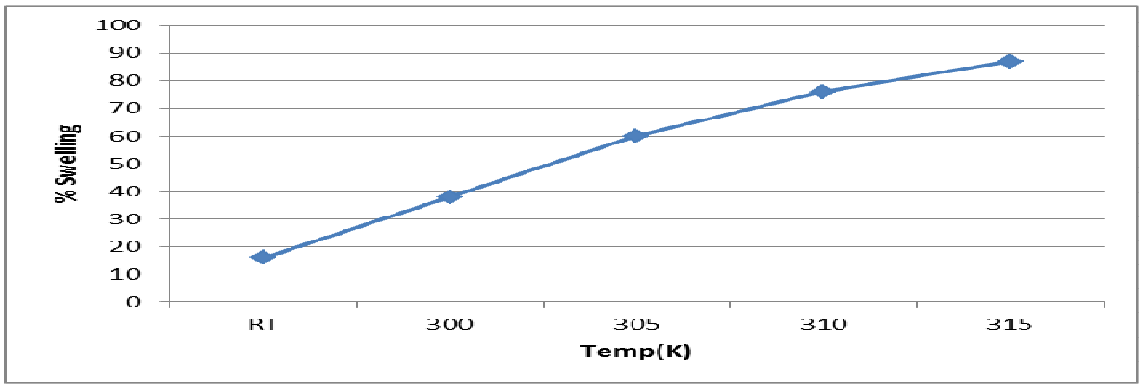
GRAPH 15
SWELLING OF HYDROGEL 1vs Temp (K)



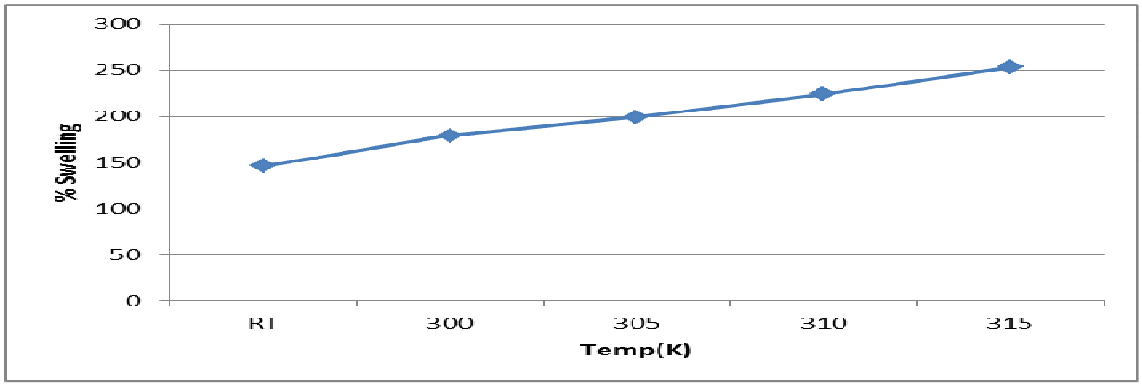
GRAPH 16
SWELLING OF HYDROGEL 2vs Temp (K)



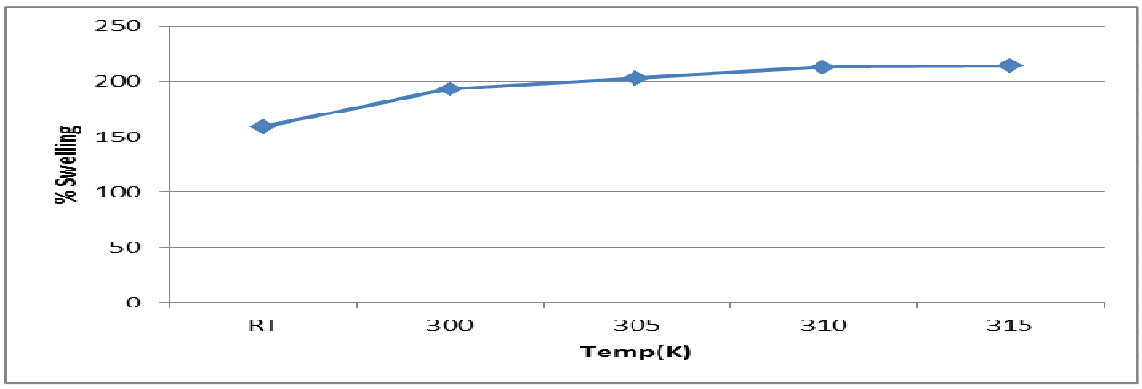
GRAPH 17
SWELLING OF HYDROGEL 3 vs Temp (K)



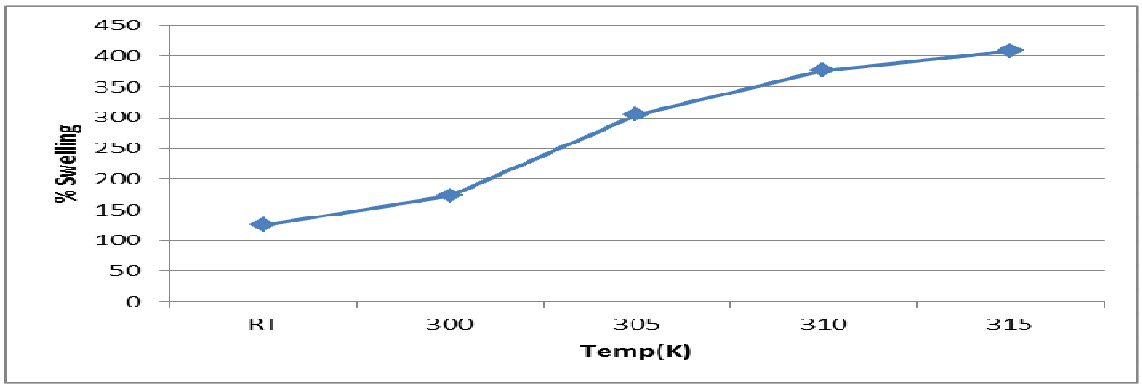
GRAPH 18
SWELLING OF HYDROGEL 4 vs Temp (K)



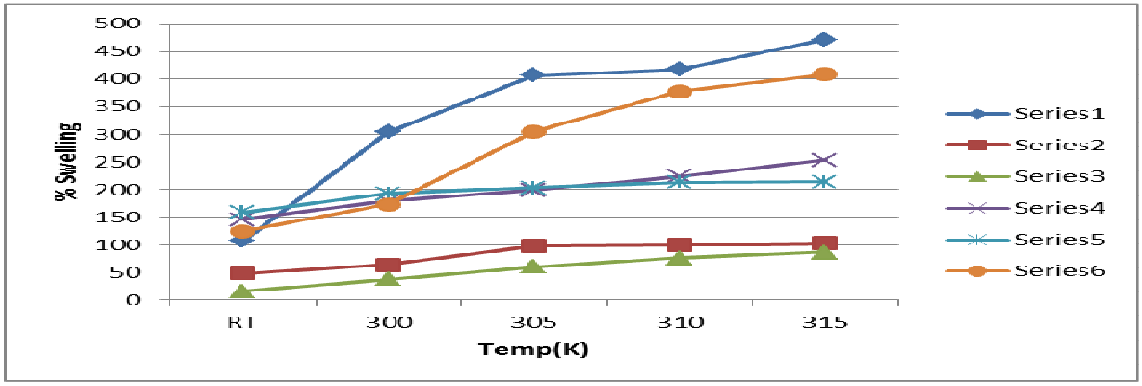
GRAPH 19
SWELLING OF HYDROGEL 5 vs Temp (K)



GRAPH 20
SWELLING OF HYDROGEL 6 vs Temp (K)



GRAPH 21
SWELLING OF HYDROGELS vs Temp (K)



CHAPTER 5

Metal Ions Uptake Study

5.1.Introduction:

The most significant field where hydrogels are finding application is environmental study and management .Treatment of water systems and removal of toxic metal ions from water is one of front line challenge. Conventional precipitation processes do not always work up to satisfactory level and synthetic ion exchange resins are quite expansive. Natural polymers like **cellulose, starch, dextran and chitosan** are extensively used in low cost technologies for the removal of metal ions from water bodies .**My attempt during the project was to use fruit juice in place of polymers above mentioned and perform the same task as it was done with the help above grafted copolymer hydrogels for metal ion uptake study**.

These polymers are of renewable origin; environmental friendly and offer highly cost effective technologies. However, utility of these polymers in membrane processes is restricted due to lack of selective binding and their high interaction leading to solubilisatoin. However graft copolymers of these polymers when used as ion exchangers, especially, as cross linked networks have advantage over the conventional ones due to low cost of preparation.

These copolymers offer large hydrophilic surface area despite being insoluble in water and enrich or separate metal ions by **binding, adsorption, chelation and ion exchange processes.**

Metal ions form complexes with polymers having anhydroglucose unit at glycolic groups[(1)]. Copolymerising of suitable monomers with hydrophobic and hydrophilic / ionic moieties combine high degree of permeability and longer stability[(2)] and enables complexation with low molecular weight surfactants both in water and low polarity media[(3)].

5.2.Review of hydrogels used in metal ion uptake

(1)Pectin and acrylamide based hydrogels have been used for the sorption of some common metal ions pollutants found in soil, industrial, and mining water bodies[(4)]

(2) Cellulosic-based hydrogels(extracted cellulose and its derivatives such as hydroxypropyl cellulose (HPC), cyanoethyl cellulose, hydroxyethyl cellulose, hydrazinodeoxy cellulose, cellulose phosphate with acrylamide (AAm) and N, N-methylene bisacrylamide synthesized by simultaneous gamma ray initiation) were used for sorption of Fe^{2+}, Cu^{2+} and Cr^{6+} ions[(5).]

(3)Hydrogels based on reaction of chitosan with polyvinyl alcohol, chitosan and polyvinyl alcohol with glutaraldehyde, N,N′-biisomaleimide, and N,N′-biisophthalimide were used for uptake of Co^{2+} and Cu^{2+} ions[(6)].

4: Hydrogels of Poly(N-acryloyl-N-ethylpiperazine) showed good uptake of divalent metal ions such as Ni^{2+}, Co^{2+}, and Zn^{2+}, with high selectivity for Ni2þ ions due to the formation of a more stable ligand-metal complex[(7)] .

5. Hydrogel obtained by grafting of Acrylamide monomer onto cellulose was used for sorption of Cu, Cr, Ni, Pb di cations [(8)]

6. Graft polymerization of polyacrylonitrile onto cellulosic material obtained from Rubber (*Hevea brasiliensis)* seed shell using ceric ammonium nitrate as initiator yields hydrogel which was used for sorption of Cr, Mn, Ni, Cu, and Pb ions [(9)].

7. Novel hydrogels based on modified cellulosics and 2-acrylamido-2-methyl propane sulphonic acid were used for sorption of Fe^{2+}, Cu^{2+} and Cr^{6+} metal ions [10].

8. N-vinylpyrrolidone/acrylic acid/2-acrylamido-2-methylpropane sulfonic acid (NVP/AAc/AMPS) based hydrogels were used to uptake Cd^{2+} , Cu^{2+} and Fe^{3+} ions from their aqueous solutions [11].

9. Hydrogel based on acrylamide and acrylic acid was synthesized and crosslinked by gamma radiation and used for uptake of Cu^{2+} [12]

10. Two chitosan hydrogels (prepared by NaOH neutralization and by polyphosphate ionotropic gelation) have been tested in the dry state for Pd^{2+} and Pt^{4+} sorption[13]

11. Sulfathiazole-based novel UV-cured hydrogel sorbents for mercury removal aqueous solutions([14]

12. Poly(3-acrylamidopropyl)trimethylammonium chloride (p(APTMACl)) hydrogels were synthesized and utilized as absorbents for the removal of toxic arsenate from aqueous medium[15]

In this chapter an attempt has been made to study the sorption of some hazardous metal ions like Hg(II),Pb(II) and Cd(II) as a function of time , pH and Temperature.

5.3.EXPERIMENTAL

5.3.1.Chemicals used for metal ion uptake study are given as follows

1: Copper Sulphate	**2: Cadmium Nitrate**
$CuSO_4.5H_2O$ [98.5%)]	$Cd(NO_3)_2$[99%]
From Qualigens Fine Chem Ltd	From Qualigens Fine Chem Ltd
M.W: 249.68	M.W: 308.48
3: Lead Nitrate	**4: Mercuric Nitrate**
$Pb(NO_3)_2$[99%]	$Hg(NO_3)_2.H_2O$[99%]
Ranbaxy	From Loba Chemi. Pvt. Ltd
M.W: 331.23	M.W: 342
5: Sodium Hydroxide	**6: PAN Indicator;**
	1-(2- Pyridinylazo)-2-Naphthol
NaOH	$C_{15}H_{11}N_3O$(0.1% Ethanol solution)
From Qualigens Fine Chem Ltd	From Loba Chemi. Pvt. Lt
M.W: 40	M.W:249.27
7: Glacial Acitic acid	**8: Sodium Acetate**
CH_3COOH	$CH_3COONa.3H_2O$[98%]
From Merck	From CDH
M.W: 60.05	M.W: 136.08
9: Ethanol	**10:EDTA Di Sodium salt**
C_2H_5OH[99.9%]	$C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$[99.5%]
From Jingasu Huaxi International Trade	From Qualigens Fine ChemLtd.Co.Ltd.
M.W: 46	M.W:372.24

In present study I have studied metal ion uptake of **Hg(II), Pb(II), and Cd(II) ions** by hydrogels prepared in Chapter No 2 by **complexometric(EDTA double Titration)** using ***0.1 % ethanolic solution of of PAN indicator*** as indicator .

5.3.2.Preparation of Solutions:

(1) Buffer solution of pH 5.2 is prepared using HENDERSON EQUATION For pH of Buffer Solutions. **[pH= pKa + log [salt]/[acid] =>(1)** ; pKa=4.75 at 25^0C

(2) 0.1% Solution of PAN indicator in Ethanol.

(3) Milimolar solution of Metal salts above mentioned and that of Copper Sulphate.

(4) Milimolar solution of EDTA di sodium salt.

Note*: All calculations for weighing were made according to equation;*

$$W = MxVxM^0 /1000 \Rightarrow (2)$$

Here M is molecular weight of substance, V is volume of solution prepared in(ml) , M^0 is molarity of solution and W is weight of substance in grams.

5.3.3.Procedure and theoretical basis for calculation of metal ion uptake in mg/gm of hydrogel.

(1) **Sorption of metal ions** :

Make dry powder of hydrogel by crushing it. Now take metal ion solution as above mentioned. Weigh a small amount of hydrogel powder nearly 0.1 grams. Take 10 ml of salt solution in a beaker of 100 ml and make volume 40 ml by adding DMW . Add powder weighed above in beaker and now let the metal be uptaken by hydrogel. Decant metal ion solution for titration when criteria allows.

(2) **Titration:** First of all fill the burette with EDTA solution mentioned above .Now take 10 ml solution of Copper Sulphate in conical flask and add 3-4 ml of buffer solution as mentioned above .Put the solution on Hot Plate till temperature is reached at 60-70^0C . Add 2-3 drop of indicator solution; a pink colour appears. If it is not pink then more heating is done. Titrate the solution in conical flask against EDTA solution and suppose volume of EDTA used for complete complex formation is V_1ml .At the end point of titration yellow coloured solution is obtained with some precipitate. Now add 10 ml solution of metal ion; taken for sorption study to the yellow coloured solution of Cu(II) –EDTA complex; so called blank ; a pink coloured solution is obtained instantly and if it is not so then heat the solution till pink coloured solution appears. Again titrate the pink coloured solution against EDTA; end point is indicated if yellow coloured solution is obtained. Suppose volume of EDTA used is V_2 ml. Now titrate the metal ion solution remained after sorption with the same procedure as above and find the volume of EDTA used .Suppose it is now V_3 ml . Thus we can calculate the equivalent volume of EDTA corresponding the amount of metal ion uptaken by hydrogel sample used. Suppose it is V ml (V_2-V_3).

(3)Calculation of metal ion uptake (mg/gm):

Here in my calculation; it is assumed that materials are pure as mentioned on pack.

By using equation **[$W = MxVxM^0 /1000$];** we can find the amount of metal ions present in 10 ml solution of metal salt taken. Suppose it is W mg. It is also assumed that W^0 mg of metal ions are completely complexed with V_2 ml of EDTA solution. Suppose amount of metal ions up taken by hydrogel taken for sorption is W mg then

$$W = VxW^0/V_2 \text{ mg} \quad => (3)$$

Now W is divided by amount of hydrogel taken for sorption to get metal ion uptake value in mg/gm of hydrogel suppose it is U.

$$U = W/W_H \quad => (4)$$

For equation (3) and (4); W is weight of metal ions in (mg) up taken by W_H gm of hydrogel sample taken for sorption study. V and V_2 have the same meaning as mentioned in procedure of titration.

5.4.Result and Discussion:

Metal ion uptake is studied as function of three parameters
(1) Time, (2) pH and (3) Temperature

5.4.1.Metal ion uptake as a function of time:

Metal ion sorption study is performed in aqueous media. Procedure is described above. Metal ions are put in contact of hydrogel for 0.5,1.0,1.5, 2.0, 3.0, 4.5, 6.5and 8 hours respectively. Now decantation is performed for finding out the amount of metal ions remained. Finally titration is performed.

5.4.2.Metal ion uptake as a function of pH:

Metal ion sorption study is performed at different pH 2,4,6,7and 8 respectively. Metal ions are put in contact of hydrogel for the best time span obtained in metal ion uptake study as a function of time. Now decantation is performed for finding out the amount of metal ions remained. Finally titration is performed.

5.4.3.Metal ion uptake as a function of Temperature:

Metal ion sorption study is performed at different Temperature; Room temperature , 27^0C, 32^0C, 37^0C, 42^0C,respectively. Metal ions are put in contact of hydrogel for the best time span obtained in metal ion uptake study as a function of time and best pH obtained in metal ion sorption as function of pH. Now decantation is performed for finding out the amount of metal ions remained. Finally titration is performed.

5.4.1.Metal ion uptake as a function of time:

From the sorption study of metal ions as function of time; one thing is clear that after a definite time interval there is slight decrease in uptake value. As we know that hydrogel uptake metal ions by **binding, adsorption, chelation and ion exchange processes.** Sorption is a reversible process so there is an increase in uptake value with time due to adsorption; but amount of metal ions on surface increases with time so there must be more repulsion for new incoming metal ions and simultaneously desorption starts so at a particular time desorption rate will competes adsorption and that is why uptake value goes down for a sort time. After this particular time again there is a continuous increase in metal ion uptake value because resultant of adsorption and desorption is not changing with time but still there are two reactions going on; chelation and ion exchange.

5.4.1.1.Hg(II) Uptake by Hydrogel vs Time

For hydrogel 1 at 1.5 hour; ultimate value is obtained and uptake value is 8.584 mg/gm after this there is slight decrease then increase in uptake value and at 8^{th} hour uptake value is 9.171 mg/gm. For hydrogel 2 at 1.5 hour; ultimate value is obtained and uptake value is 10.36mg/gm which is greater than that of hydrogel 1 .This is because of the fact that there are more polar groups in hydrogel because it is a copolymer of Acrylamide and Acrylic acid; after this there is slight decrease then increase in uptake value and at 8^{th} hour uptake value is 11.209 mg/gm. For hydrogel 3 at 2 hour; ultimate value is obtained and uptake value is 14.125 mg/gm which is greater than that of hydrogel 1; even at 1 hour value is greater .This is because of the fact that there are more polar groups in hydrogel 3 because it is a copolymer of Acrylamide and Methacrylic acid ; after this there is slight decrease and then increase in uptake value and at 8^{th} hour uptake value is 16.106 mg/gm. Thus over all hydrogel 3 is better than both 1&2 regarding uptake value.

For hydrogel 4 which is Acrylamide and sugar based ultimate value is obtained at 2 hours and value is 10.408 mg/gm after this there is slight decrease and then increase in uptake value and at 8^{th} hour uptake value is 11.696 mg/gm. Thus it is also better for Hg(II) sorption in comparision to Homo polymer of Acrylamide and it is perhaps due to presence of additional hydroxyl groups in the network. For hydrogel 5 ultimate value is 9.057 mg/gm and it is reached at 2 hours after this there is slight decrease and then increase in uptake value and at 8^{th} hour uptake value is 11.075 mg/gm. Thus it is slight better than homo polymer but not much difference perhaps due lesser amount of polarity in respect to hydrogel 4. For hydrogel 6 after 2 hours value obtained is 16.786 mg/gm ; after this there is only slight decrease for 3^{rd} hour and then much increase in uptake value and at 8^{th} hour uptake value is 20.644 mg/gm. Thus hydrogel 6 is best

among all hydrogels in my project for Hg(II) sorption . This indicates there may be more polar groups present in this hydrogel.

5.4.1.2.Pb(II) Uptake by Hydrogels vs Time

For hydrogel 1 ultimate value is obtained at1hour and it is 3.666 mg/gm. After this much decrease in uptake value till 4.5 hour and after this slight increase is reported at 8^{th} hour value is 4.056 mg/gm. For hydrogel 2 ultimate value is 3.426 mg/gm and it is at 1 hour after there is a decrease and finally over value 8^{th} hour is 3.563 mg/gm .In the case of hydrogel 3 ; uptake value at 1 hour is ultimate and it is 3.452 mg/gm after that there is a decrease and finally over value 8^{th} hour is 7.708 mg/gm. Thus it is best absorber for Pb(II) among fully synthetic hydrogels. For hydrogel 4 ;value after 2 hour is 9.408 mg/gm after that decrease in value till 4.5 hours then value increases and at 8 hour value is 8.589 mg/gm .thus for hydrogel 4 max value is at 2 hours . For hydrogel 5 value at 2 hours is 6.328 mg/gm and that trend is as usual and value at 8^{th} hour is 6.68 mg/gm. Finally for hydrogel 6 value regarding Pb(II) ion at 1.5 hour is ultimate and at 8^{th} hour value is 6.262 mg/gm .Thus for Pb(II) sorption hydrogel 4 is found best and philicity towards metal ion sorption by hydrogels is more for Hg(II) than Pb(II). From above results it is clear that mechanism of Pb(II) ion sorption may be more towards adsorption and very less towards chelation or ion exchange.

5.4.1.3.Cd(II) Uptake by Hydrogels vs Time

For hydrogel 1 ; value of cadmium ion uptake at 2 hours is ultimate because after this there is decrease in uptake value and then increase in it and at 8^{th} hour value is 3.349 mg/gm while at 2^{nd} hour it was 2.902. For hydrogel 2; value of cadmium ion uptake at 2 hours is 2.429 which is ultimate because after this there is decrease in uptake value and then increase in it; and at 8^{th} hour value is 2.741mg/gm. For hydrogel 3; value of cadmium ion uptake at1.5 hours is 3.883which is ultimate because after this there is decrease in uptake value and then increase in it; and at 8^{th} hour value is 4.425 mg/gm. Thus hydrogel 3 is best for Cd(II) ion uptake among synthetic . For hydrogel 4; value of cadmium ion uptake at 2 hours is ultimate because after this there is decrease in uptake value and then increase in it and at 8^{th} hour value is 7.101 mg/gm while at 2^{nd} hour it was 6.532 mg/gm. Thus hydrogel 4 is better for the purpose than synthetic hydrogels. For hydrogel 5; value of cadmium ion uptake at 1 hours is 4.117which is ultimate because after this there is decrease in uptake value and then increase in it; and at 8^{th} hour value is 4.485mg/gm. . For hydrogel 6; value of cadmium ion uptake at 1.5 hours is ultimate because after this there is decrease in uptake value and then increase in it and at 8^{th} hour value is 5.681mg/gm while at 1.5^{th} hour it was 4.756 mg/gm. Thus hydrogel 4 is best for the purpose among all hydrogels.
Thus over result is that hydrogels are more effective for Hg(II) and least for Pb(II).

5.4.2.Metal ion uptake as a function of pH:

From overall sorption result of hydrogels as function of pH ; it seen that at lower pH value of U is lower generally least and increases with pH but minimum at pH 7 and again increases with pH and in most of the cases max at pH 8. It is due to the fact that at lower pH generally polarity is destroyed by H^+ ions and it competes with metal ions

due to smaller size .As pH rises; there is decrease in H^+ ion concentration so U value rises .At pH 7 ;generally no H^+ ion is present for competition with metal ions so value must be highest but there are more hydrogen bonding and lesser availability of polarity so lesser uptake of metal ions. When pH rises from7 ;then due to basic media hydrolysis of functional groups takes place hence more polar groups are available for binding now U value should increase and in most of the cases it is found so.

5.4.2.1.Hg(II) Uptake by Hydrogel vs pH

For hydrogel 1; U value is minimum at pH 2 (5.204) and rises with pH; ultimate at pH 6(17.627) which is max ; deceases at pH 7 (8.584) again greater at pH 8. For hydrogel 2; U value is minimum at pH 2 (2.576) and rises with pH; ultimate at pH4(20.591) after which deceases at pH 7 (10.027) again greater at pH 8(25.84) which is max . Overall it is better pH responsive than hydrogel 1. For hydrogel 3; U value is minimum at pH 2 (9.326) and rises with pH; ultimate at pH4(19.548) after which deceases at pH 7 (14.126) again greater at pH 8(23.656) which is max. For hydrogel 4; U value is minimum at pH 2 (4.689) and rises with pH; ultimate at pH6 (16.973) after which deceases at pH 7 (9.912) again greater at pH 8(31.746) which is max. For hydrogel 5; U value is minimum at pH 2 (8.674) and rises with pH; ultimate at pH6 (27.858) which is max. After which deceases at pH 7 (9.057) again greater at pH 8(18.215). For hydrogel 6; U value is minimum at pH 2 (13.038) and rises with pH; ultimate at pH6 (19.429) which is max. After which deceases at pH 7 (15.715) again greater at pH 8(17.122) . Thus Hydrogel based on sugar are more pH responsive than synthetic .

5.4.2.2.Pb(II) Uptake by Hydrogel vs pH

Regarding Pb(II); sorption values are very small in pH lower than 7 but max at pH For hydrogel 1; U value is minimum at pH 2 (0.992) and rises with pH; ultimate at pH 8(35.426) which is max ; deceases at pH 7 (3.366) . Thus hydrogel 1 shows great response to medium change. For hydrogel 2; U value is minimum at pH 2 (1.043) and rises with pH; ultimate at pH 8(18.054) which is max; deceases at pH 7 (3.426) . Thus hydrogel shows lesser response to medium change than hydrogel 1. For hydrogel 3; U value is minimum at pH 2 (0.636) and rises with pH; ultimate at pH 8(21.869) which is max; deceases at pH 7 (3.542). Thus hydrogel shows lesser response to medium change than hydrogel 1 but better than hydrogel 2. For hydrogel 4; U value is minimum at pH 2 (1.358) and rises with pH; ultimate at pH 8(20.449) which is max; Thus hydrogel shows continuous response to medium change. For hydrogel 5; U value is minimum at pH 2 (1.012) and rises with pH; ultimate at pH 8(20.411) which is max; deceases at pH 7 (6.328). For hydrogel 6; U value is minimum at pH 2 (2.062) and rises with pH; ultimate at pH 4 (5.741) which is max; deceases from here.

5.4.2.3.Cd (II) Uptake by Hydrogel vs pH

For hydrogel 1;U value is 3.577 at pH 2 .It increases with pH and then decreases becomes minimum at pH 7(2.638) ;ultimate value is at pH 8 (14.049) which is max. . For hydrogel 2; U value is 3.737at pH 2 and rises with pH and then decreases becomes minimum at pH 7(2.429) ; ultimate at pH 8(14.802) which is max . For

hydrogel 3; U value is 3.322 at pH 2 and it is minimum and rises with pH and then decreases and at pH 7(3.883) ; ultimate at pH 8(14.802) which is max . For hydrogel 4 U is zero at pH 2 and increases with pH and then decreases. U value is ultimate at pH 6(7.868).For Hydrogel 5; U value is minimum at pH 2(0.944) .It increases with pH and then decreases. Value is ultimate at pH 8(12.744) which is max. For hydrogel 6; U value is 10.939 at pH 2 and it is ultimate value. U value decreases becomes minimum at pH 6(4.211).Now value increases and max at pH 8(15.753)

5.4.3.Metal ion uptake as a function of Temperature:

From sorption study as a function of temperature; it is clear that there is an ultimate temperature around 30^0 C. At this temperature sorption is maximum and below or above this temperature sorption value decreases. It is because of the fact that for each reaction there is an ultimate temperature.

5.4.3.1.Hg(II) Uptake by Hydrogel vs Temperature:

For hydrogel 1; U value is maximum at 27^0C(23.13) ;after this U value decreases. Simlerly for hydrogel 2 ,3 ,4 ,5 & 6 maximum values are at R.T(25.84) ,27^0C(22.418) , 27^0C(32.888), R.T(27.858) , 27^0C(23.679) respectively.
Regarding sorption of Hg(II); Hydrogel 4&6 are much thermo responsive.

5.4.3.2.Pb(II) Uptake by Hydrogel vs Temperature:

Regarding sorption of Pb(II) ; Hydrogel 1 has maximum U value at R.T(35.42)
Simlerly for hydrogel 2,3 ,4 ,5 & 6 maximum values are at , 27^0C(31.07) , 27^0C(30.773), 32^0C(29.272), R.T (20.411), &27^0C (10.844) respectively.

5.4.3.3.Cd(II) Uptake by Hydrogel vs Temperature:

Regarding sorption of Cd(II) ; Hydrogel 1 has maximum U value at R.T(14.049)
Simlerly for hydrogel 2,3 ,4 ,5 & 6 maximum values are at , R.T(14.505) , R.T(12.911), 32^0C(11.443), 27^0C (13.191), &27^0C (18.121) respectively. Thus for sorption as function of temperature there is definite temperature at which value is maximum.

METAL ION UPTAKE RESULT OF HYDROGEL IN TABULER FORM

TABLE 1

Hg(II) Uptake by Hydrogel 1 vs Time

S.No	Time(hr)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	0.5	0.162	9.5	6.6	2.9	6.521
2	1	0.137	9.5	6.3	3.2	8.509
3	1.5	0.174	9.5	5.4	4.1	8.584
4	2	0.151	9.5	6.1	3.4	8.203
5	3	0.132	9.5	6.3	3.2	8.831
6	4.5	0.162	9.5	5.5	4	8.995
7	6.5	0.141	9.5	6	3.5	9.042
8	8	0.143	9.5	5.9	3.6	9.171

TABLE2

Hg(II) uptake by hydrogel 2 vs time

S.No	Time(hr)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	0.5	0.073	9.5	8.3	1.2	5.988
2	1	0.069	9.5	7.6	1.9	10.031
3	1.5	0.109	9.5	6.4	3.1	10.36
4	2	0.06	9.5	7.8	1.7	10.321
5	3	0.133	9.5	5.7	3.8	10.409
6	4.5	0.065	9.5	7.6	1.9	10.649
7	6.5	0.076	9.5	7.2	2.3	11.024
8	8	0.08	9.5	6.7	2.8	11.209

TABLE3

Hg(II) uptake by hydrogel 3 vs time

S.No	Time(hr)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	0.5	0.135	9.5	7.6	1.9	5.127
2	1	0.112	9.5	5.5	4	11.944
3	1.5	0.126	9.5	5.1	4.4	12.722
4	2	0.147	9.5	3.8	5.7	14.125
5	3	0.096	9.5	5.8	3.7	14.04
6	4.5	0.099	9.5	5.5	4	14.719
7	6.5	0.093	9.5	5.5	4	15.669
8	8	0.095	9.5	5.3	4.2	16.106

TABLE4

Hg (II)uptake by hydrogel 4 vs time

S.No	Time(hr)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	0.5	0.119	9.5	7	2.5	7.693
2	1	0.144	9.5	5.6	3.9	9.866
3	1.5	0.127	9.5	5.9	3.6	10.326
4	2	0.147	9.5	5.3	4.2	10.408
5	3	0.11	9.5	5.4	3.1	10.226
6	4.5	0.124	9.5	5.8	3.7	10.87
7	6.5	0.195	9.5	3.5	6	11.209
8	8	0.19	9.5	3.4	6.1	11.696

TABLE5

Hg (II)uptake by hydrogel 5 vs time

S.No	Time(hr)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	0.5	0.148	9.5	6.5	3	7.384
2	1	0.141	9.5	6.3	3.2	8.268
3	1.5	0.107	9.5	6.9	2.6	8.852
4	2	0.181	9.5	5	4.5	9.057
5	3	0.159	9.5	5.8	3.7	8.706
6	4.5	0.162	9.5	5.1	4.4	9.895
7	6.5	0.128	9.5	5.8	3.7	10.531
8	8	0.125	9.5	5.7	3.8	11.075

TABLE6

Hg(II) uptake by hydrogel6 vs time

S.No	**Time(hr)**	**W1(gm)**	**V1(ml)**	**V2(ml)**	**V(ml)**	**U(mg/gm)**
1	**0.5**	**0.105**	**9.5**	**7.3**	**2.2**	**7.632**
2	**1**	**0.083**	**9.5**	**6.9**	**2.6**	**11.412**
3	**1.5**	**0.085**	**9.5**	**5.5**	**4**	**16.217**
4	**2**	**0.102**	**9.5**	**4.8**	**4.7**	**16.786**
5	**3**	**0.076**	**9.5**	**6**	**3.5**	**16.746**
6	**4.5**	**0.059**	**9.5**	**6.4**	**3.1**	**19.141**
7	**6.5**	**0.058**	**9.5**	**6.3**	**3.2**	**20.099**
8	**8**	**0.06**	**9.5**	**6.1**	**3.4**	**20.644**

TABLE7

Pb(II) Uptake by Hydrogel 1 vs Time

S.No	Time(hr)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	0.5	0.139	10	9	1	2.403
2	1	0.164	10	8.2	1.8	3.666
3	1.5	0.14	10	8.8	1.2	2.863
4	2	0.166	10	9	1	2.012
5	3	0.166	10	8.5	1.5	3.018
6	4.5	0.152	10	8.4	1.6	3.515
7	6.5	0.152	10	8.2	1.8	3.955
8	8	0.142	10	8.3	1.7	4.056

TABLE8

Pb(II) Uptake by Hydrogel 2 vs Time

S.No	Time(hr)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	0.5	0.166	10	9.5	0.5	1.006
2	1	0.156	10	8.4	1.6	3.426
3	1.5	0.159	10	8.5	1.5	3.15
4	2	0.157	10	8.6	1.4	2.978
5	3	0.152	10	8.7	1.3	3.076
6	4.5	0.158	10	8.4	1.6	3.382
7	6.5	0.157	10	8.4	1.6	3.404
8	8	0.15	10	8.4	1.6	3.563

TABLE9

Pb(II) Uptake by Hydrogel 3 vs Time

S.No	Time(hr)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	0.5	0.139	10	9.2	0.8	1.922
2	1	0.132	10	8.6	1.4	3.452
3	1.5	0.128	10	8.7	1.3	3.392
4	2	0.135	10	8.6	1.4	3.464
5	3	0.129	10	8.2	1.8	4.66
6	4.5	0.129	10	8.1	1.9	4.919
7	6.5	0.135	10	7	3	7.422
8	8	0.13	10	7	3	7.708

TABLE10

Pb(II) Uptake by Hydrogel 4 vs Time

S.No	Time(hr)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	0.5	0.081	10	9.7	0.3	1.237
2	1	0.071	10	8.6	1.4	6.586
3	1.5	0.074	10	8.2	1.8	8.124
4	2	0.071	10	8	2	9.408
5	3	0.074	10	8.6	1.4	6.319
6	4.5	0.072	10	8.8	1.2	5.567
7	6.5	0.068	10	8.4	1.6	7.858
8	8	0.07	10	8.2	1.8	8.589

TABLE11

Pb(II) Uptake by Hydrogel 5 vs Time

S.No	Time(hr)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	0.5	0.104	10	9	1	3.212
2	1	0.096	10	8.5	1.5	5.219
3	1.5	0.095	10	8.3	1.7	5.977
4	2	0.095	10	8.2	1.8	6.328
5	3	0.097	10	8.5	1.5	5.765
6	4.5	0.098	10	8.2	1.8	6.135
7	6.5	0.095	10	8.2	1.8	6.328
8	8	0.09	10	8.2	1.8	6.68

TABLE12

Pb(II) Uptake by Hydrogel 6 vs Time

S.No	Time(hr)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	0.5	0.076	10	9.3	0.7	3.076
2	1	0.082	10	8.8	1.2	4.888
3	1.5	0.082	10	8.7	1.3	5.295
4	2	0.089	10	9	1	3.753
5	3	0.081	10	8.8	1.2	4.948
6	4.5	0.086	10	8.7	1.3	5.048
7	6.5	0.085	10	8.5	1.5	5.894
8	8	0.08	10	8.5	1.5	6.262

TABLE13

Cd(II) Uptake by Hydrogel 1 vs Time

S.No	Time(hr)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	0.5	0.12	9.6	9	0.6	1.495
2	1	0.178	9.6	8.5	1.1	1.848
3	1.5	0.129	9.6	8.6	1	2.318
4	2	0.102	9.6	8.5	1.1	2.902
5	3	0.168	9.6	8.1	1.5	2.67
6	4.5	0.125	9.6	8.4	1.2	2.87
7	6.5	0.134	9.6	8.2	1.4	3.124
8	8	0.125	9.6	8.2	1.4	3.349

TABLE14

Cd(II) Uptake by Hydrogel 2 vs Time

S.No	Time(hr)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	0.5	0.206	9.6	8.8	0.8	1.161
2	1	0.193	9.6	8.6	1	1.549
3	1.5	0.202	9.6	8	1.6	2.368
4	2	0.16	9.6	8.3	1.3	2.429
5	3	0.17	9.6	8.3	1.3	2.286
6	4.5	0.123	9.6	8.6	1	2.431
7	6.5	0.119	9.6	8.6	1	2.513
8	8	0.12	9.6	8.5	1.1	2.741

TABLE15

Cd(II) Uptake by Hydrogel 3 vs Time

S.No	Time(hr)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	0.5	0.198	9.6	9	0.6	0.906
2	1	0.282	9.6	7.6	2	2.121
3	1.5	0.077	9.6	8.6	1	3.883
4	2	0.082	9.6	8.6	1	3.646
5	3	0.086	9.6	8.5	1.1	3.824
6	4.5	0.101	9.6	8.2	1.4	4.145
7	6.5	0.216	9.6	6.5	3.1	4.291
8	8	0.12	9.6	7.8	1.8	4.425

TABLE16

Cd(II) Uptake by Hydrogel 4 vs Time

S.No	Time(hr)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	0.5	0.073	9.6	8.7	0.9	3.686
2	1	0.155	9.6	7	2.6	5.015
3	1.5	0.111	9.6	7.2	2.4	6.465
4	2	0.119	9.6	7	2.6	6.532
5	3	0.117	9.6	7.1	2.5	6.389
6	4.5	0.093	9.6	7.5	2.1	6.751
7	6.5	0.072	9.6	7.4	2.2	6.997
8	8	0.08	9.6	7.7	1.9	7.101

TABLE17

Cd(II) Uptake by Hydrogel 5 vs Time

S.No	Time(hr)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	0.5	0.13	9.6	8.6	1	2.3
2	1	0.138	9.6	7.7	1.9	4.117
3	1.5	0.25	9.6	6.6	3	3.477
4	2	0.145	9.6	7.6	2	4.124
5	3	0.226	9.6	6.5	3.1	4.101
6	4.5	0.252	9.6	6.1	3.5	4.152
7	6.5	0.187	9.6	6.9	2.7	4.317
8	8	0.1	9.6	8.1	1.5	4.485

TABLE18

Cd(II) Uptake by Hydrogel 10 vs Time

S.No	Time(hr)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	0.5	0.122	9.6	9.1	0.5	1.225
2	1	0.102	9.6	8.1	1.5	4.397
3	1.5	0.088	9.6	8.2	1.4	4.756
4	2	0.077	9.6	8.4	1.2	4.659
5	3	0.106	9.6	7.9	1.7	4.795
6	4.5	0.08	9.6	8.2	1.4	5.232
7	6.5	0.067	9.6	8.4	1.2	5.355
8	8	0.1	9.6	7.7	1.9	5.681

TABLE19

Hg(II) Uptake by Hydrogel 1 vs pH

S.No	pH	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	2	0.133	9.5	7.6	1.9	5.204
2	4	0.095	9.5	5.5	4	15.339
3	6	0.093	9.5	5	4.5	17.627
4	7	0.174	9.5	4.1	4.1	8.584
5	8	0.093	9.5	4.3	4.3	16.844

TABLE 20

Hg(II) Uptake by Hydrogel 2 vs pH

S.No	pH	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	2	0.099	9.5	8.8	0.7	2.576
2	4	0.092	9.5	4.3	5.2	20.591
3	6	0.102	9.5	4.5	5	17.857
4	7	0.109	9.5	6.5	3	10.027
5	8	0.086	9.5	3.4	6.1	25.84

TABLE 21

Hg(II) Uptake by Hydrogel 3 vs pH

S.No	pH	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	2	0.125	9.5	6.3	3.2	9.326
2	4	0.082	9.5	5.1	4.4	19.548
3	6	0.086	9.5	5.9	3.6	18.215
4	7	0.147	9.5	3.8	5.7	14.126
5	8	0.077	9.5	4.5	5	23.656

TABLE 22

Hg(II) Uptake by Hydrogel 4 vs pH

S.No	pH	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	2	0.101	9.5	8.2	1.3	4.689
2	4	0.084	9.5	6.6	2.9	12.577
3	6	0.088	9.5	5.4	4.1	16.973
4	7	0.147	9.5	5.5	4	9.912
5	8	0.07	9.5	3.4	6.1	31.746

TABLE 23

Hg(II) Uptake by Hydrogel 5 vs pH

S.No	pH	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	2	0.105	9.5	7	2.5	8.674
2	4	0.071	9.5	5.1	4.4	22.576
3	6	0.075	9.5	3	6.5	27.858
4	7	0.181	9.5	5	4.5	9.057
5	8	0.078	9.5	5.6	3.9	18.215

TABLE 24

Hg(II) Uptake by Hydrogel 6 vs pH

S.No	pH	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	2	0.095	9.5	6.1	3.4	13.038
2	4	0.09	9.5	4.9	4.6	18.62
3	6	0.105	9.5	3.9	5.6	19.429
4	7	0.102	9.5	5.1	4.4	15.715
5	8	0.1	9.5	4.8	4.7	17.122

TABLE 25

Pb(II) Uptake by Hydrogel 1 vs pH

S.No	pH	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	2	0.101	10	9.7	0.3	0.992
2	4	0.096	10	9	1	3.479
3	6	0.096	10	8.6	1.4	5.221
4	7	0.164	10	8.2	1.8	3.366
5	8	0.066	10	3	7	35.426

TABLE 26

Pb(II) Uptake by Hydrogel 2 vs pH

S.No	pH	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	2	0.096	10	9.7	0.3	1.043
2	4	0.092	10	9	1	3.63
3	6	0.097	10	8.2	1.8	6.198
4	7	0.156	10	8.4	1.6	3.426
5	8	0.074	10	6	4	18.054

TABLE27

Pb(II) Uptake by Hydrogel 3 vs pH

S.No	pH	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	2	0.105	10	9.8	0.2	0.636
2	4	0.081	10	8.9	1.1	4.536
3	6	0.075	10	9.2	0.8	3.562
4	7	0.132	10	8.6	1.4	3.542
5	8	0.084	10	4.5	5.5	21.869

TABLE28

Pb(II) Uptake by Hydrogel 4 vs pH

S.No	pH	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	2	0.123	10	9.5	0.5	1.358
2	4	0.106	10	9	1	3.151
3	6	0.117	10	8.5	1.5	4.282
4	7	0.071	10	8	2	9.408
5	8	0.098	10	4	6	20.449

TABLE29

Pb(II) Uptake by Hydrogel 5 vs pH

S.No	pH	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	2	0.099	10	9.7	0.3	1.012
2	4	0.085	10	8.8	1.2	4.715
3	6	0.081	10	8.2	1.8	7.422
4	7	0.095	10	8.2	1.8	6.328
5	8	0.072	10	5.6	4.4	20.411

TABLE 30

Pb(II) Uptake by Hydrogel 6 vs pH

S.No	pH	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	2	0.081	10	9.5	0.5	2.062
2	4	0.064	10	8.9	1.1	5.741
3	6	0.101	10	8.3	1.7	5.621
4	7	0.082	10	8.7	1.3	5.295
5	8	0.092	10	8.7	1.3	4.72

TABLE31

Cd(II) Uptake by Hydrogel 1 vs pH

S.No	pH	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	2	0.117	9.6	8.2	1.4	3.577
2	4	0.093	9.6	7.6	2	6.43
3	6	0.096	9.6	8.1	1.5	4.672
4	7	0.102	9.6	8.7	0.9	2.638
5	8	0.083	9.6	5.7	3.9	14.049

TABLE32

Cd(II) Uptake by Hydrogel 2 vs pH

S.No	pH	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	2	0.12	9.6	8.1	1.5	3.737
2	4	0.102	9.6	6.4	3.2	9.38
3	6	0.092	9.6	7.5	2.1	6.825
4	7	0.16	9.6	8.3	1.3	2.429
5	8	0.101	9.6	4.6	5	14.802

TABLE 33

Cd(II) Uptake by Hydrogel 3 vs pH

S.No	pH	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	2	0.126	9.6	8.2	1.4	3.322
2	4	0.088	9.6	8.3	1.3	4.417
3	6	0.095	9.6	8.3	1.3	4.091
4	7	0.077	9.6	8.6	1	3.883
5	8	0.088	9.6	5.8	3.8	12.911

TABLE 34

Cd(II) Uptake by Hydrogel 4vs pH

S.No	pH	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	2	0.109	9.6	9.6	0	0
2	4	0.087	9.6	8.2	1.4	4.867
3	6	0.076	9.6	7.6	2	7.868
4	7	0.119	9.6	7	2.6	6.532
5	8	0.074	9.6	9.6	0	0

TABLE35

Cd(II) Uptake by Hydrogel 5vs pH

S.No	pH	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	2	0.095	9.6	9.3	0.3	0.944
2	4	0.108	9.6	7.8	1.8	4.983
3	6	0.112	9.6	8.4	1.2	3.203
4	7	0.138	9.6	7.7	1.9	4.116
5	8	0.061	9.6	7	2.6	12.744

TABLE 36

Cd(II) Uptake by Hydrogel 6vs pH

S.No	pH	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	2	0.082	9.6	6.6	3	10.939
2	4	0.089	9.6	8.1	1.5	5.039
3	6	0.071	9.6	8.6	1	4.211
4	7	0.088	9.6	8.2	1.4	4.756
5	8	0.093	9.6	4.7	4.9	15.753

TABLE 37

Hg(II) Uptake by Hydrogel 1 vs Temp

S.No	Temp(K)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	R.T	0.093	9.5	5	4.5	17.627
2	300	0.063	9.5	5.5	4	23.13
3	305	0.065	9.5	6.5	3	16.813
4	310	0.064	9.5	7	2.5	14.23
5	315	0.07	9.5	7.4	2.1	10.929

TABLE 38

Hg(II) Uptake by Hydrogel 2 vs Temp

S.No	Temp(K)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	R.T	0.086	9.5	3.4	6.1	25.84
2	300	0.085	9.5	4.5	5	21.429
3	305	0.072	9.5	6	3.5	17.709
4	310	0.073	9.5	6.5	3	14.971
5	315	0.085	9.5	6.6	2.9	12.429

TABLE 39

Hg(II) Uptake by Hydrogel 3 vs Temp

S.No	Temp(K)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	R.T	0.082	9.5	5.1	4.4	19.548
2	300	0.078	9.5	4.7	4.8	22.418
3	305	0.069	9.5	6	3.5	18.479
4	310	0.085	9.5	6.8	2.7	11.572
5	315	0.074	9.5	7.2	2.3	11.322

TABLE 40

Hg(II) Uptake by Hydrogel 4vs Temp

S.No	Temp(K)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	R.T	0.07	9.5	3.4	6.1	31.746
2	300	0.072	9.5	3	6.5	32.888
3	305	0.066	9.5	5	4.5	24.839
4	310	0.066	9.5	5.6	3.9	21.527
5	315	0.073	9.5	6	3.5	17.466

TABLE 41

Hg(II) Uptake by Hydrogel 5vs Temp

S.No	Temp(K)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	R.T	0.085	9.5	3	6.5	27.858
2	300	0.066	9.5	5	4.5	24.839
3	305	0.07	9.5	5.5	4	20.817
4	310	0.074	9.5	5.7	3.8	18.707
5	315	0.08	9.5	6.5	3	13.661

TABLE 42

Hg(II) Uptake by Hydrogel 6vs Temp

S.No	Temp(K)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	R.T	0.105	9.5	3.9	5.6	19.429
2	300	0.08	9.5	4.3	5.2	23.679
3	305	0.089	9.5	5.5	4	16.373
4	310	0.074	9.5	6.5	3	14.769
5	315	0.07	9.5	7.9	2.6	13.531

TABLE 43

Pb(II) Uptake by Hydrogel 1 vs Temp

S.No	Temp(K)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	R.T	0.066	10	3	7	35.42
2	300	0.074	10	2.5	7.5	33.851
3	305	0.069	10	3.4	6.6	31.948
4	310	0.067	10	5	5	24.925
5	315	0.063	10	7.5	2.5	13.254

TABLE 44

Pb(II) Uptake by Hydrogel 2 vs Temp

S.No	Temp(K)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	R.T	0.074	10	6	4	18.054
2	300	0.086	10	2	8	31.07
3	305	0.081	10	4	6	24.741
4	310	0.068	10	5.2	4.8	23.576
5	315	0.09	10	7	3	11.133

TABLE 45

Pb(II) Uptake by Hydrogel 3 vs Temp

S.No	Temp(K)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	R.T	0.084	10	4.5	5.5	21.869
2	300	0.089	10	1.8	8.2	30.773
3	305	0.066	10	4	6	30.363
4	310	0.098	10	5.9	4.1	13.973
5	315	0.072	10	7	3	13.916

TABLE 46

Pb(II) Uptake by Hydrogel 4vs Temp

S.No	Temp(K)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	R.T	0.098	10	4	6	20.449
2	300	0.082	10	4.6	5.4	21.955
3	305	0.089	10	2.2	7.8	29.272
4	310	0.09	10	5	5	18.555
5	315	0.078	10	5.7	4.3	18.412

TABLE 47

Pb(II) Uptake by Hydrogel 5vs Temp

S.No	Temp(K)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	R.T	0.074	10	5.6	4.4	20.411
2	300	0.086	10	5.2	4.8	18.642
3	305	0.076	10	6.2	3.8	16.7
4	310	0.064	10	7.4	2.6	13.568
5	315	0.074	10	7	3	13.54

TABLE 48

Pb(II) Uptake by Hydrogel 6vs Temp

S.No	Temp(K)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	R.T	0.081	10	8.9	1.1	5.741
2	300	0.077	10	7.5	2.5	10.844
3	305	0.079	10	7.8	2.2	9.301
4	310	0.08	10	8.3	1.7	7.097
5	315	0.061	10	8.8	1.2	6.57

TABLE 49

Cd(II) Uptake by Hydrogel 1 vs Temp

S.No	Temp(K)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	R.T	0.083	9.6	5.7	3.9	14.049
2	300	0.066	9.6	7	2.6	11.779
3	305	0.077	9.6	6.7	2.9	11.226
4	310	0.089	9.6	6.5	3.1	10.415
5	315	0.072	9.6	7.3	2.3	9.551

TABLE50

Cd(II) Uptake by Hydrogel 2 vs Temp

S.No	Temp(K)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	R.T	0.101	9.6	4.7	4.9	14.505
2	300	0.063	9.6	6.7	2.7	13.763
3	305	0.087	9.6	6.4	3.2	10.998
4	310	0.068	9.6	7.6	2	8.794
5	315	0.09	9.6	7.5	2.5	8.306

TABLE51

Cd(II) Uptake by Hydrogel 3 vs Temp

S.No	Temp(K)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	R.T	0.088	9.6	5.8	3.8	12.911
2	300	0.077	9.6	7	2.6	10.096
3	305	0.075	9.6	7.4	2.2	8.771
4	310	0.076	9.6	7.5	2.1	8.261
5	315	0.063	9.6	8	1.6	7.593

TABLE 52

Cd(II) Uptake by Hydrogel 4vs Temp

S.No	Temp(K)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	R.T	0.076	9.6	7.6	2	7.868
2	300	0.082	9.6	7.2	2.4	8.757
3	305	0.081	9.6	6.5	3.1	11.443
4	310	0.073	9.6	7.4	2.2	9.011
5	315	0.076	9.6	7.8	1.8	7.082

TABLE 53

Cd(II) Uptake by Hydrogel 5vs Temp

S.No	Temp(K)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	R.T	0.061	9.6	7	2.6	12.744
2	300	0.068	9.6	6.6	3	13.191
3	305	0.079	9.6	6.2	3.4	12.868
4	310	0.098	9.6	7	2.6	7.933
5	315	0.077	9.6	8	1.6	6.213

TABLE 54

Cd(II) Uptake by Hydrogel 6vs Temp

S.No	Temp(K)	W1(gm)	V1(ml)	V2(ml)	V(ml)	U(mg/gm)
1	R.T	0.093	9.6	5.1	4.5	14.467
2	300	0.066	9.6	5.6	4	18.121
3	305	0.06	9.6	6.5	3.1	15.448
4	310	0.081	9.6	7.1	2.5	9.228
5	315	0.071	9.6	8.8	8.8	3.369

TABLE 55
Hg(II) UPTAKE BY HYDROGEL vs TIME

Time(hr)	U1(mg/gm)	U2(mg/gm)	U3(mg/gm)	U4(mg/gm)	U5(mg/gm)	U6mg/gm)
0.5	6.521	5.988	5.127	7.693	7.384	7.632
1	8.509	10.031	11.944	9.866	8.268	11.412
1.5	8.584	10.36	12.722	10.326	8.852	16.217
2	8.203	10.321	14.125	10.408	9.057	16.786
3	8.831	10.409	14.04	10.226	8.706	16.746
4.5	8.995	10.649	14.719	10.87	9.895	19.141
6.5	9.042	11.024	15.669	11.209	10.531	20.099
8	9.171	11.209	16.106	11.696	11.075	20.644

TABLE 56

Pb(II) UPTAKE BY HYDROGEL vs TIME

Time(hr)	U1(mg/gm)	U2(mg/gm)	U3(mg/gm)	U4(mg/gm)	U5(mg/gm)	U6(mg/gm)
0.5	2.403	1.006	1.922	1.237	3.212	3.076
1	3.666	3.426	3.452	6.586	5.219	4.888
1.5	2.863	3.15	3.392	8.124	5.977	5.295
2	2.012	2.978	3.464	9.408	6.328	3.753
3	3.018	3.076	4.66	6.319	5.765	4.948
4.5	3.515	3.382	4.919	5.567	6.135	5.048
6.5	3.955	3.404	7.422	7.858	6.328	5.894
8	4.056	3.563	7.708	8.589	6.68	6.262

TABLE57

Cd(II) UPTAKE BY HYDROGEL vs TIME

Time(hr)	U1(mg/gm)	U2(mg/gm)	U3(mg/gm)	U4(mg/gm)	U5(mg/gm)	U6(mg/gm)
0.5	1.495	1.161	0.906	3.686	2.3	1.225
1	1.848	1.549	2.121	5.015	4.117	4.397
1.5	2.318	2.368	3.883	6.465	3.477	4.756
2	2.902	2.429	3.646	6.532	4.124	4.659
3	2.67	2.286	3.824	6.389	4.101	4.795
4.5	2.87	2.431	4.145	6.751	4.152	5.232
6.5	3.124	2.513	4.291	6.997	4.317	5.355
8	3.349	2.741	4.425	7.101	4.485	5.681

TABLE58

Hg(II) UPTAKE BY HYDROGEL vs pH

pH	U1(mg/gm)	U2(mg/gm)	U3(mg/gm)	U4(mg/gm)	U5(mg/gm)	U6(mg/gm)
2	5.204	2.576	9.326	4.689	8.674	13.038
4	15.339	20.591	19.548	12.577	22.576	18.62
6	17.627	17.857	18.215	16.973	27.858	19.429
7	8.584	10.027	14.126	9.912	9.057	15.715
8	16.844	25.84	23.656	31.746	18.215	17.122

TABLE59

Pb(II) UPTAKE BY HYDROGEL vs pH

pH	U1(mg/gm)	U2(mg/gm)	U3(mg/gm)	U4(mg/gm)	U5(mg/gm)	U6(mg/gm)
2	0.992	1.043	0.636	1.358	1.012	2.062
4	3.479	3.63	4.536	3.151	4.715	5.741
6	5.221	6.198	3.562	4.282	7.422	5.621
7	3.366	3.426	3.542	9.408	6.328	5.295
8	35.426	18.054	21.869	20.449	20.411	4.72

TABLE60

Cd(II) UPTAKE BY HYDROGEL vs pH

pH	U1(mg/gm)	U2(mg/gm)	U3(mg/gm)	U4(mg/gm)	U5(mg/gm)	U6(mg/gm)
2	3.577	3.737	3.322	0	0.944	10.939
4	6.43	9.38	4.417	4.867	4.983	5.039
6	4.672	6.825	4.091	7.868	3.203	4.211
7	2.638	2.429	3.883	6.532	4.116	4.756
8	14.049	14.802	12.911	0	12.744	15.753

TABLE61

Hg(II) UPTAKE BY HYDROGEL vs TEMP

Temp(K)	U1(mg/gm)	U2(mg/gm)	U3(mg/gm)	U4(mg/gm)	U5(mg/gm)	U6(mg/gm)
R.T	17.627	25.84	19.548	31.746	27.858	19.429
300	23.13	21.429	22.418	32.888	24.839	23.679
305	16.813	17.709	18.479	24.839	20.817	16.373
310	14.23	14.971	11.572	21.527	18.707	14.769
315	10.929	12.429	11.322	17.466	13.661	13.531

TABLE62

Pb(II) UPTAKE BY HYDROGEL vs TEMP

Temp(K)	U1(mg/gm)	U2(mg/gm)	U3(mg/gm)	U4(mg/gm)	U5(mg/gm)	U6(mg/gm)
R.T	35.42	18.054	21.869	20.449	20.411	5.741
300	33.851	31.07	30.773	21.955	18.642	10.844
305	31.948	24.741	30.363	29.272	16.7	9.301
310	24.925	23.576	13.973	18.555	13.568	7.097
315	13.254	11.133	13.916	18.412	13.54	6.57

TABLE63

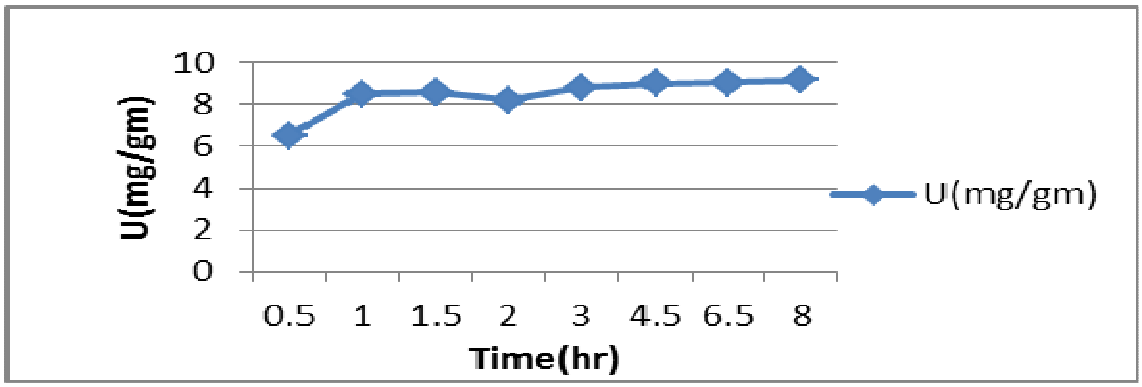
Cd(II) UPTAKE BY HYDROGEL vs TEMP

Temp(K)	U1(mg/gm)	U2(mg/gm)	U3(mg/gm)	U4(mg/gm)	U5(mg/gm)	U6(mg/gm)
R.T	14.049	14.505	12.911	7.868	12.744	14.467
300	11.779	13.763	10.096	8.757	13.191	18.121
305	11.226	10.998	8.771	11.443	12.868	15.448
310	10.415	8.794	8.261	9.011	7.933	9.228
315	9.551	8.306	7.593	7.082	6.213	3.369

METAL ION UPTAKE RESULT OF HYDROGEL IN GRAPHICAL FORM

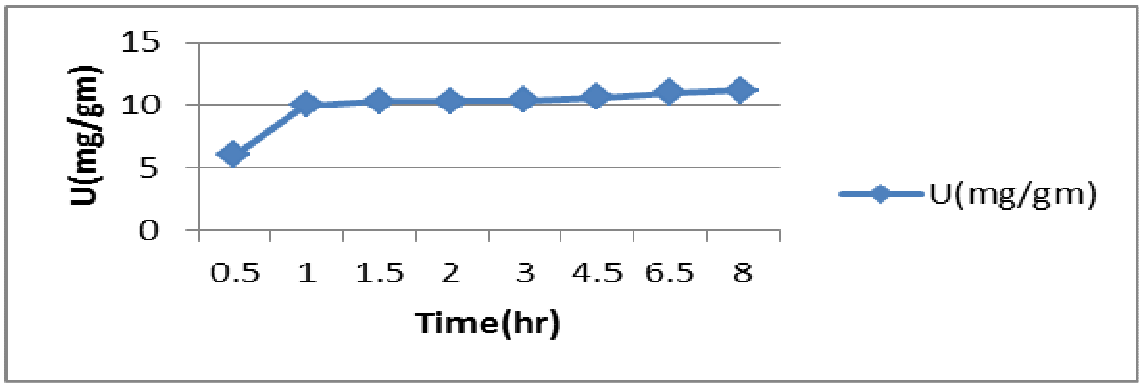
GRAPH 1

Hg(II) Uptake by Hydrogel 1 vs time



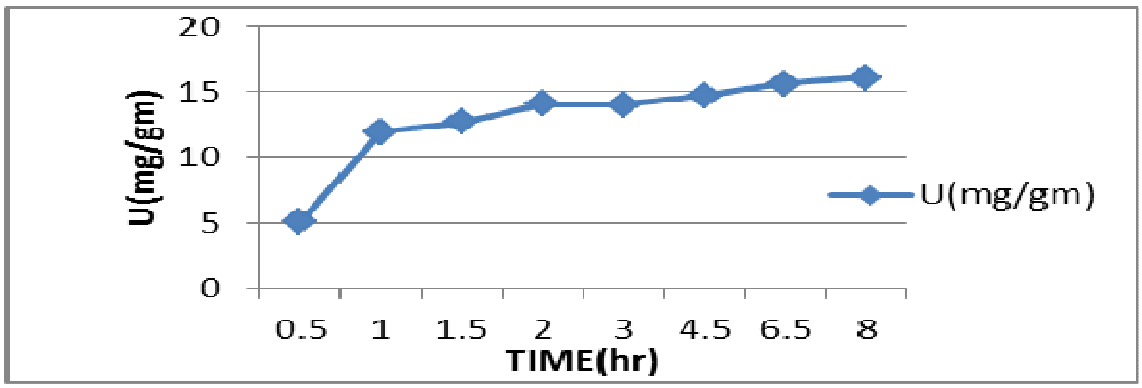
GRAPH 2

Hg(II) uptake by hydrogel 2 vs time



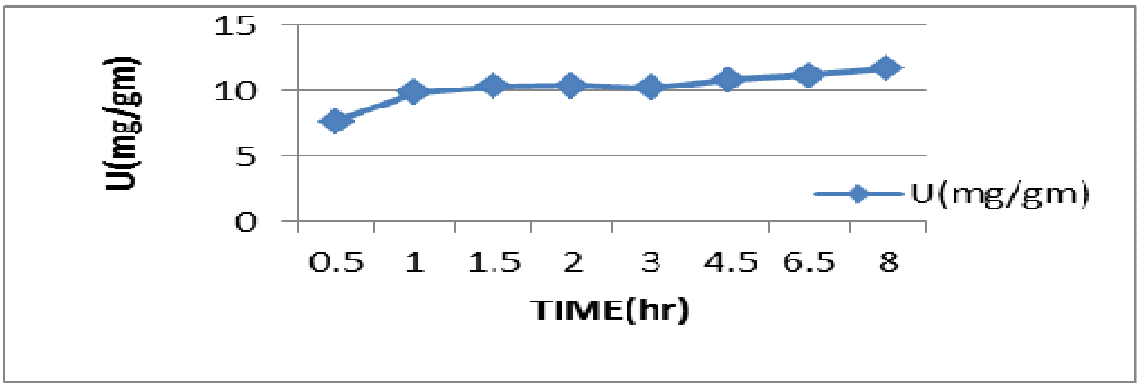
GRAPH3

Hg(II) uptake by hydrogel 3 vs time



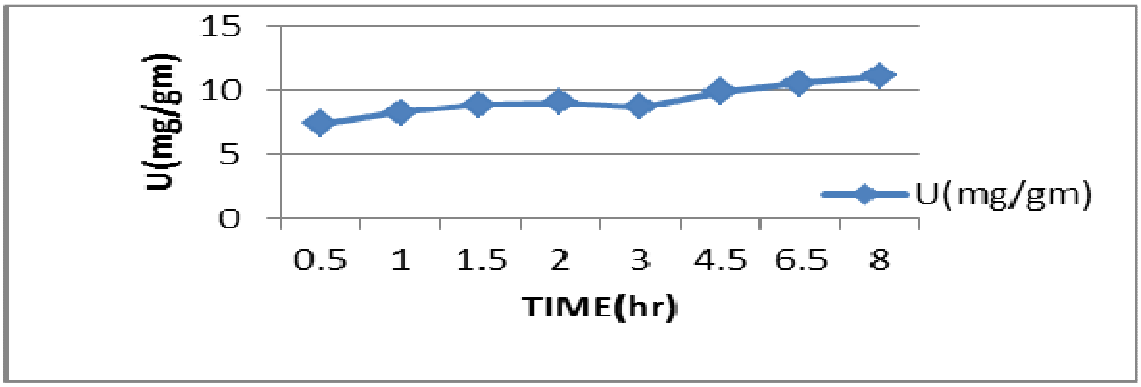
GRAPH 4

Hg(II) uptake by hydrogel 4 vs time



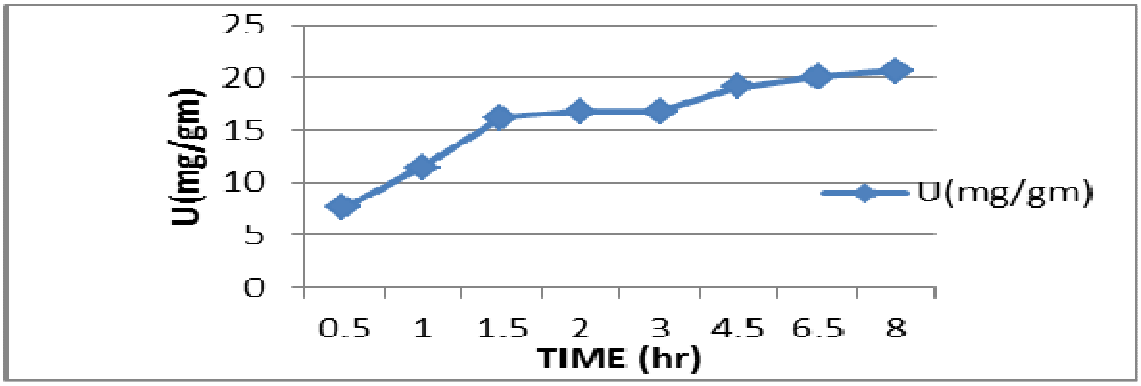
GRAPH 5

Hg(II) uptake by hydrogel 5 vs time



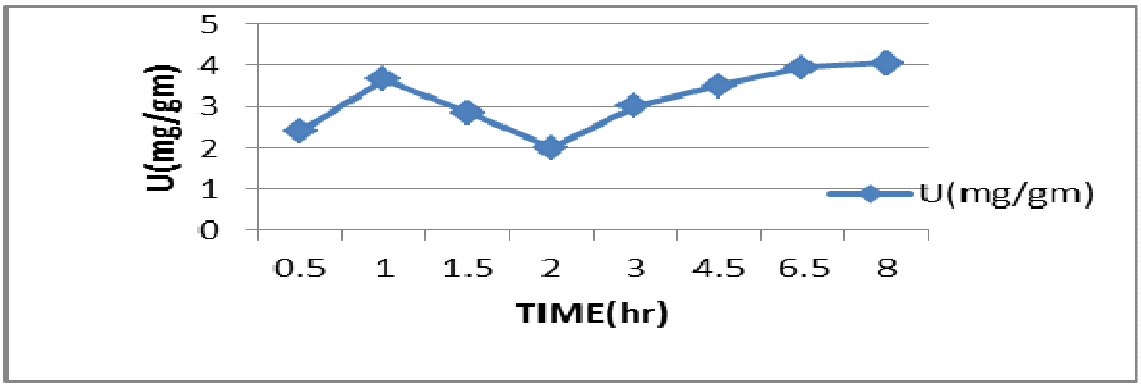
GRAPH 6

Hg(II) uptake by hydrogel 6 vs time



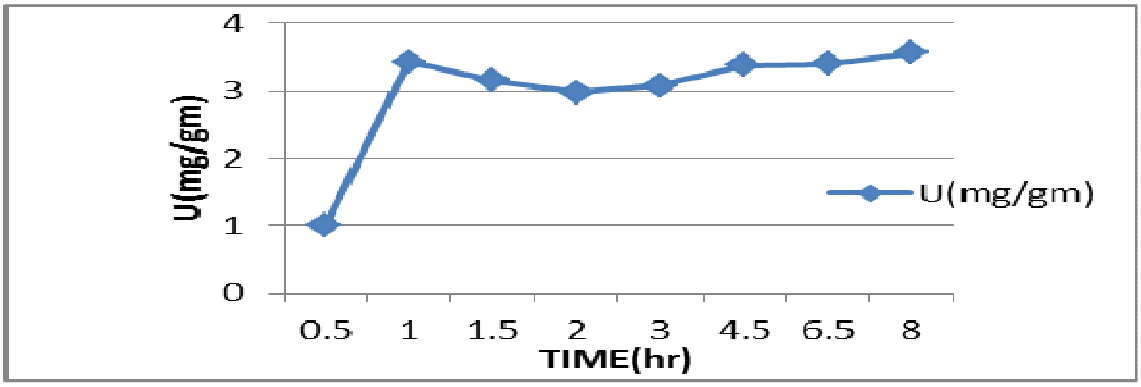
GRAPH 7

Pb(II) uptake by hydrogel 1 vs time



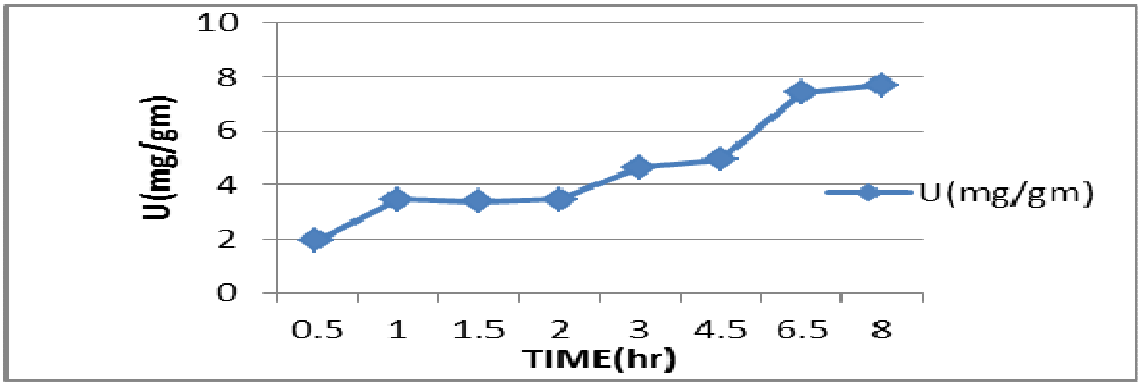
GRAPH 8

Pb(II) uptake by hydrogel 2 vs time



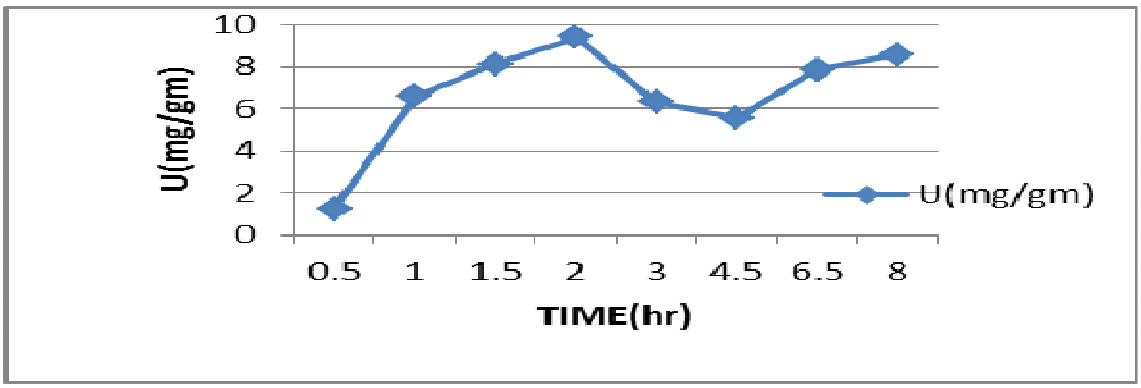
GRAPH 9

Pb(II) uptake by hydrogel 3 vs time



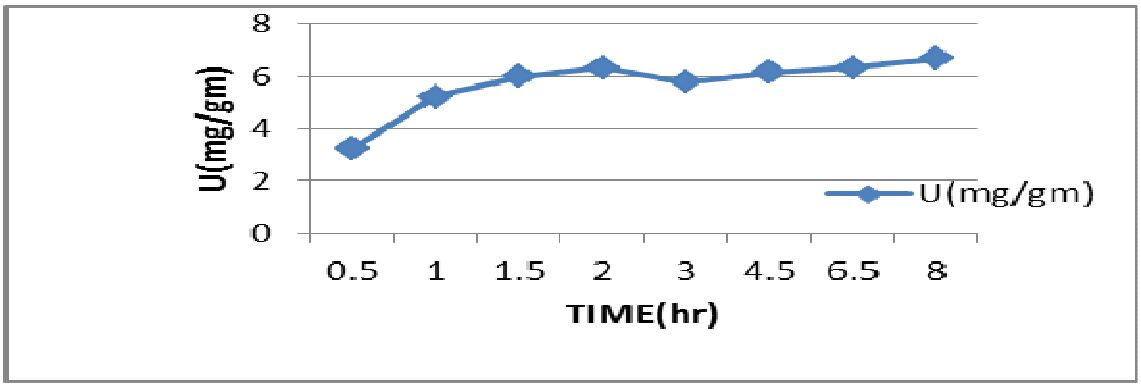
GRAPH 10

Pb(II) uptake by hydrogel 4 vs time



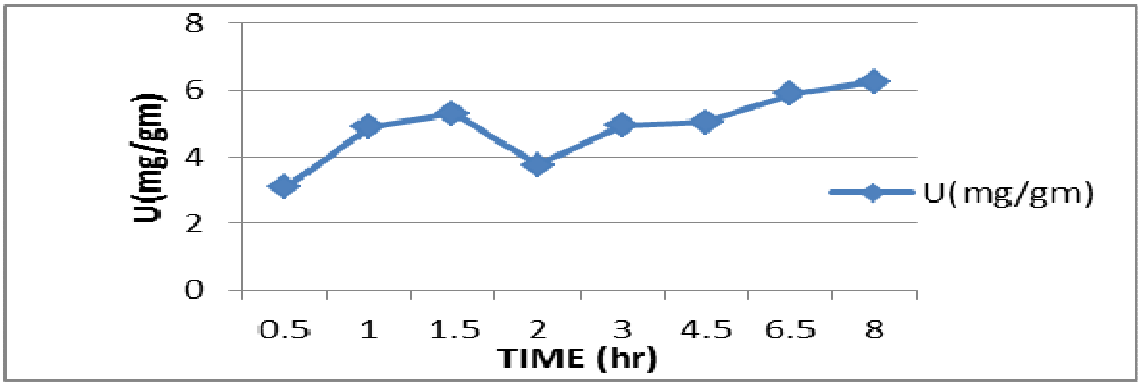
GRAPH 11

Pb(II) uptake by hydrogel 5 vs time



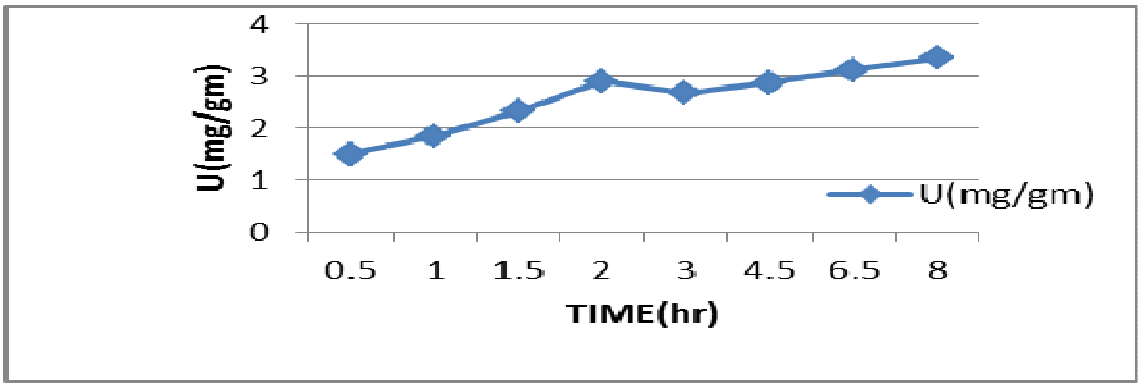
GRAPH 12

Pb(II) uptake by hydrogel 6 vs time



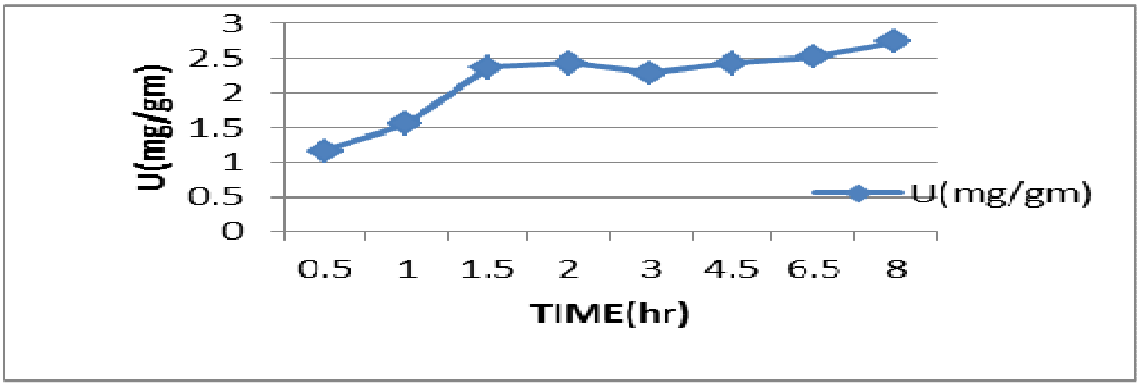
GRAPH 13

Cd(II) uptake by hydrogel 1 vs time



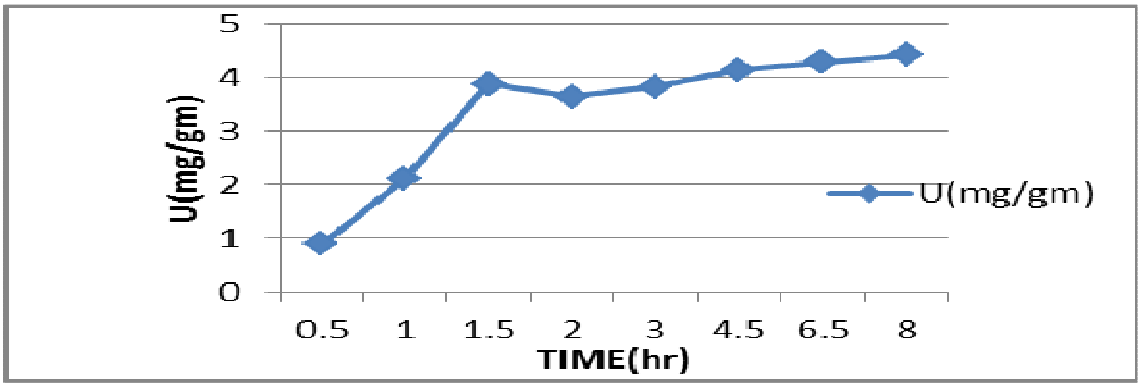
GRAPH 14

Cd(II) uptake by hydrogel 2 vs time



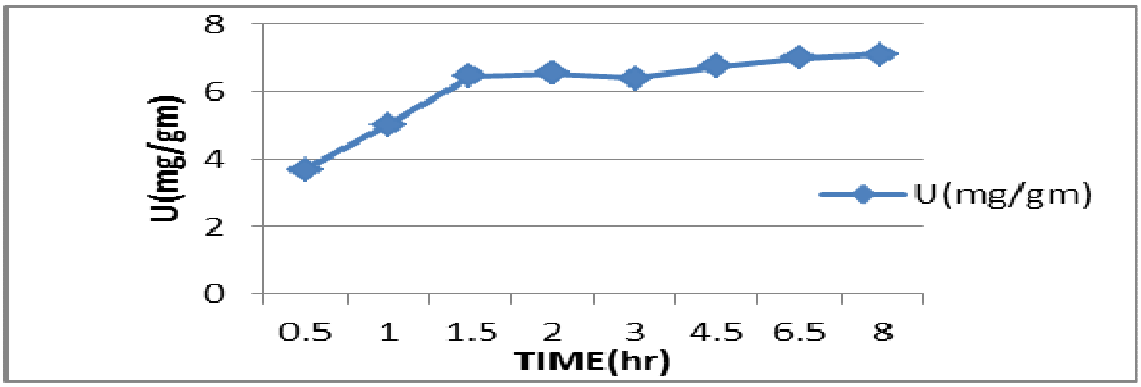
GRAPH 15

Cd(II) uptake by hydrogel 3 vs time



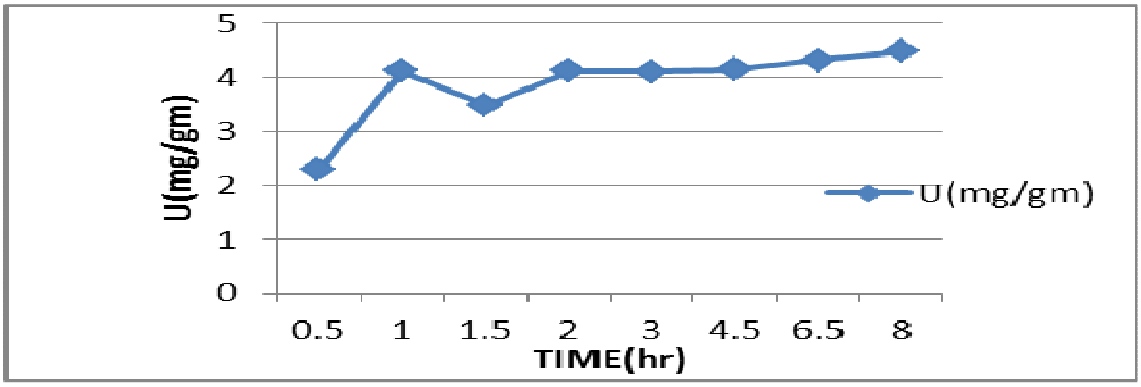
GRAPH 16

Cd(II) uptake by hydrogel 4vs time



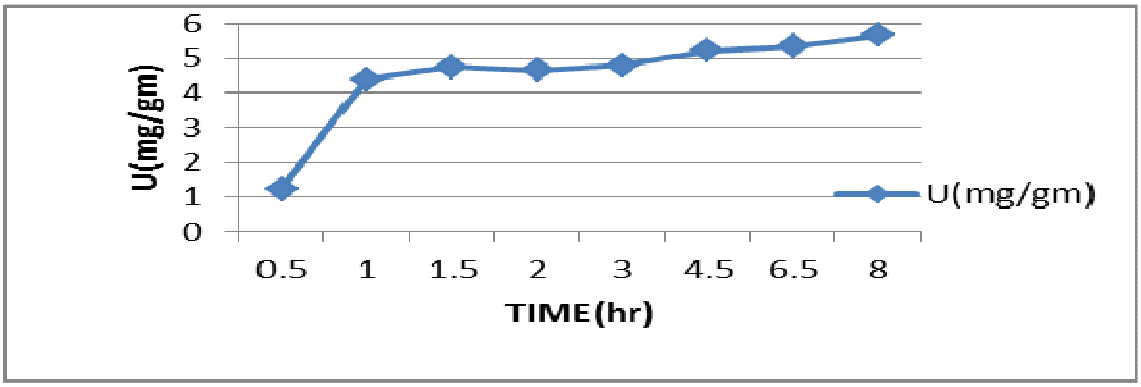
GRAPH 17

Cd(II) uptake by hydrogel 5vs time



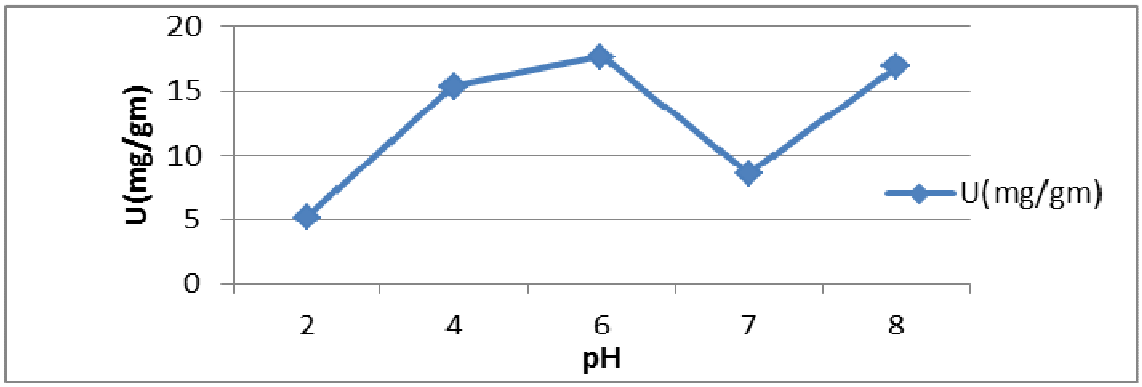
GRAPH 18

Cd(II) uptake by hydrogel 6vs time



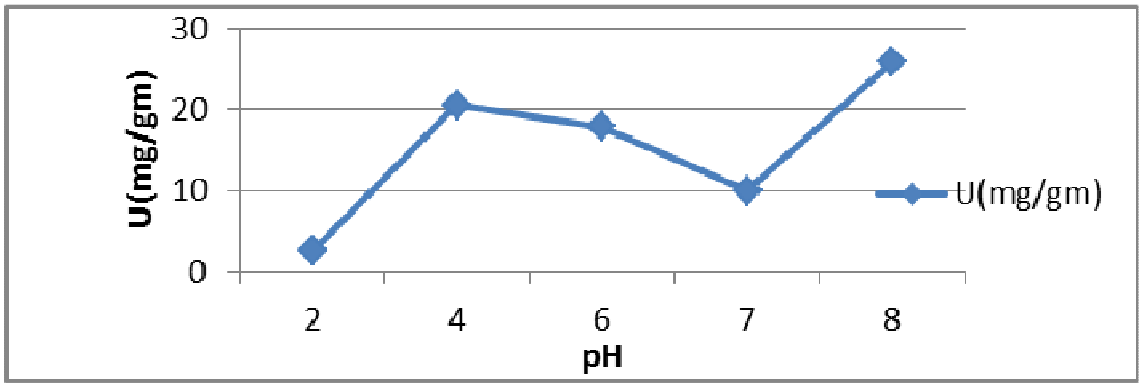
GRAPH 19

Hg(II) uptake by hydrogel 1vs pH



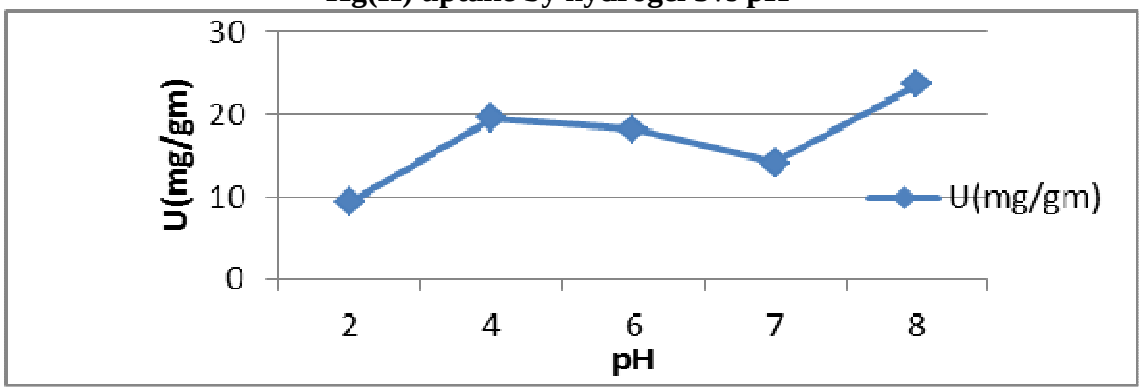
GRAPH 20

Hg(II) uptake by hydrogel 2vs pH



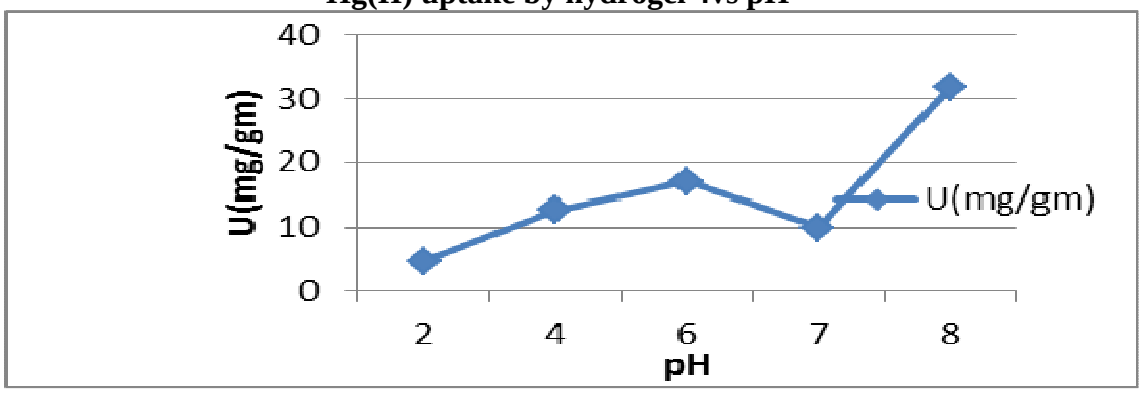
GRAPH 21

Hg(II) uptake by hydrogel 3vs pH



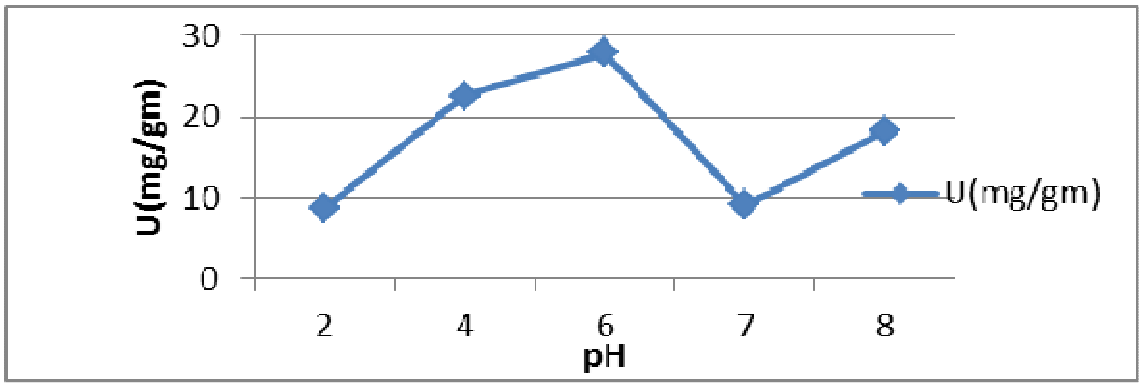
GRAPH 22

Hg(II) uptake by hydrogel 4vs pH



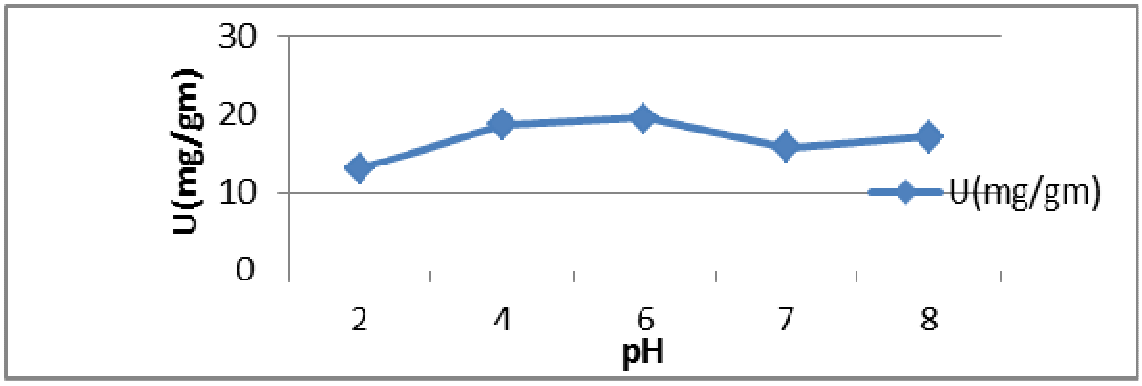
GRAPH 23

Hg(II) uptake by hydrogel 5vs pH



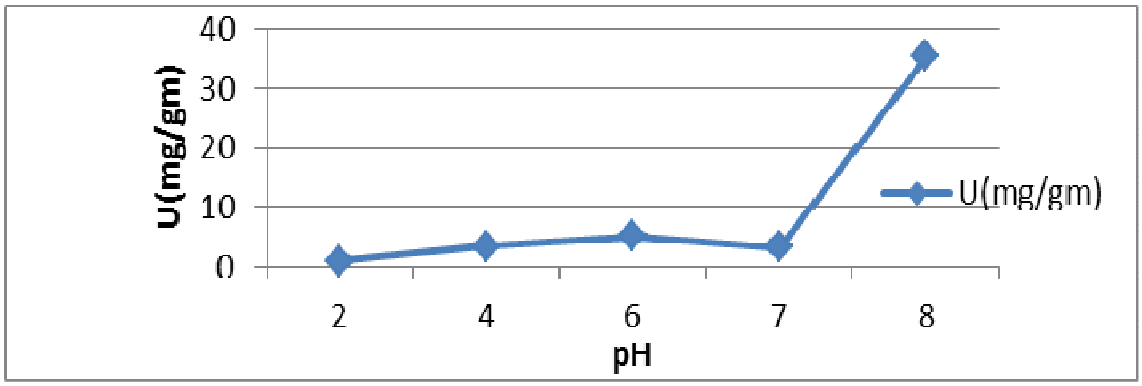
GRAPH 24

Hg(II) uptake by hydrogel 6vs pH



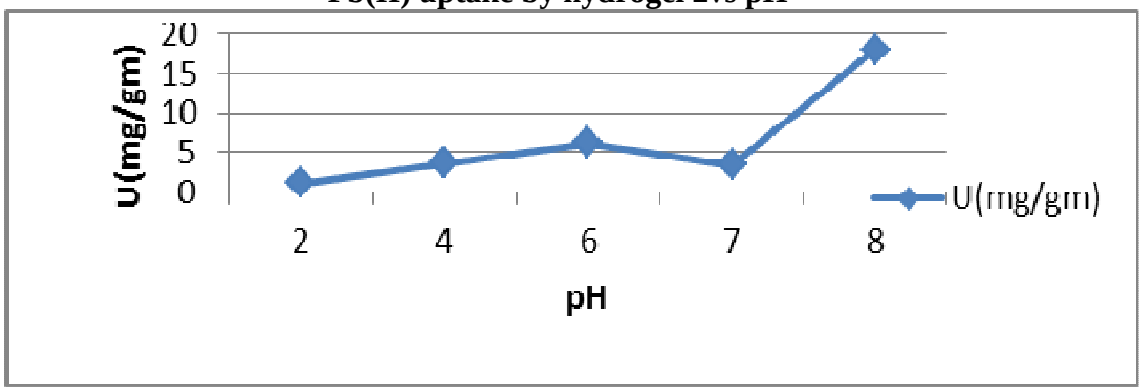
GRAPH 25

Pb(II) uptake by hydrogel 1vs pH



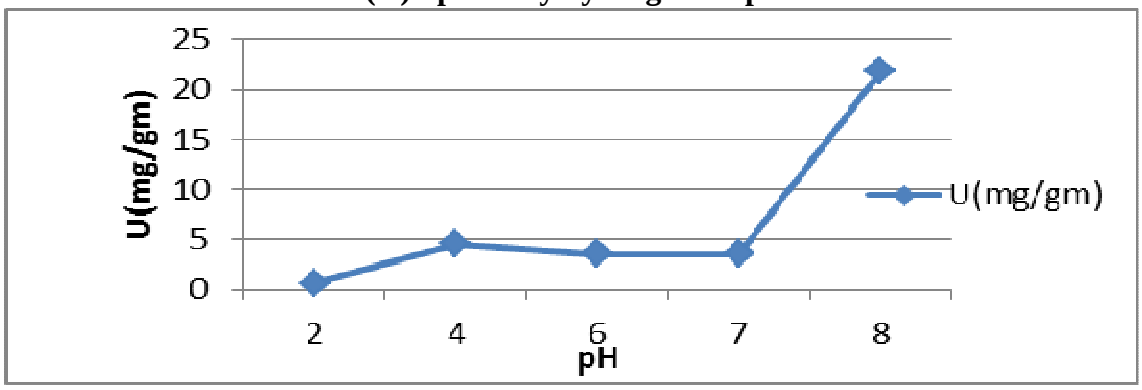
GRAPH 26

Pb(II) uptake by hydrogel 2vs pH



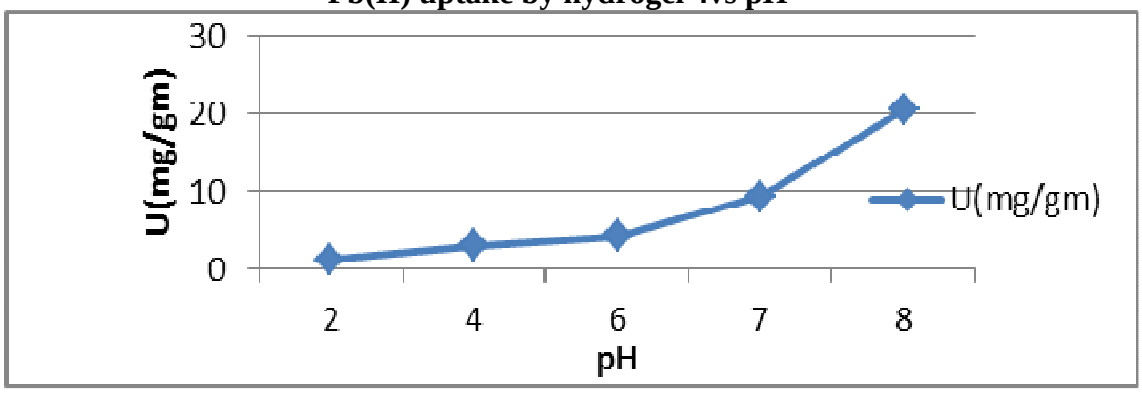
GRAPH 27

Pb(II) uptake by hydrogel 3vs pH



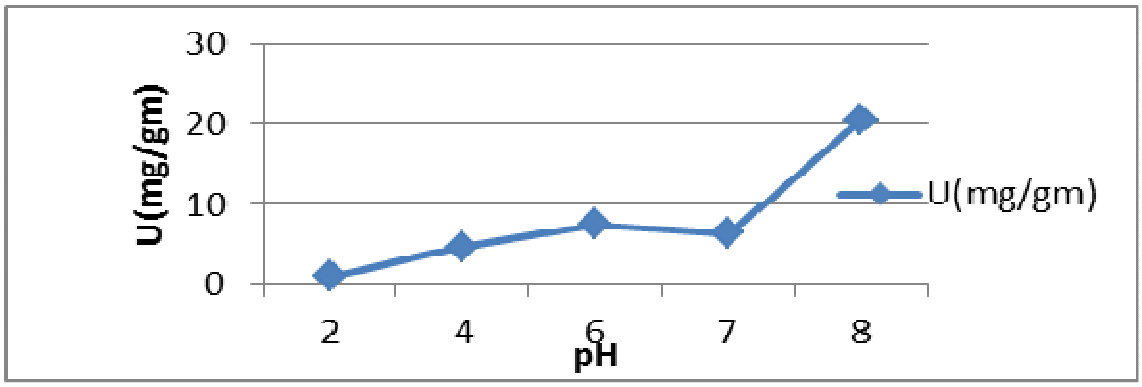
GRAPH 28

Pb(II) uptake by hydrogel 4vs pH



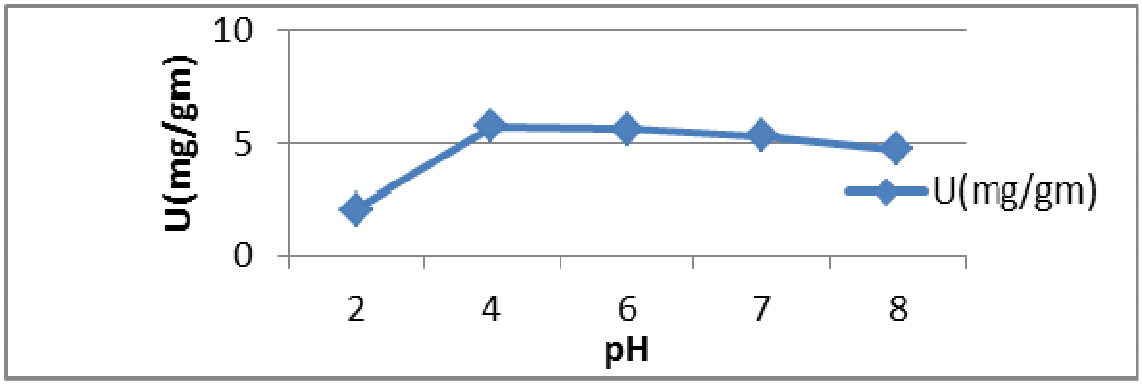
GRAPH 29

Pb(II) uptake by hydrogel 5vs pH



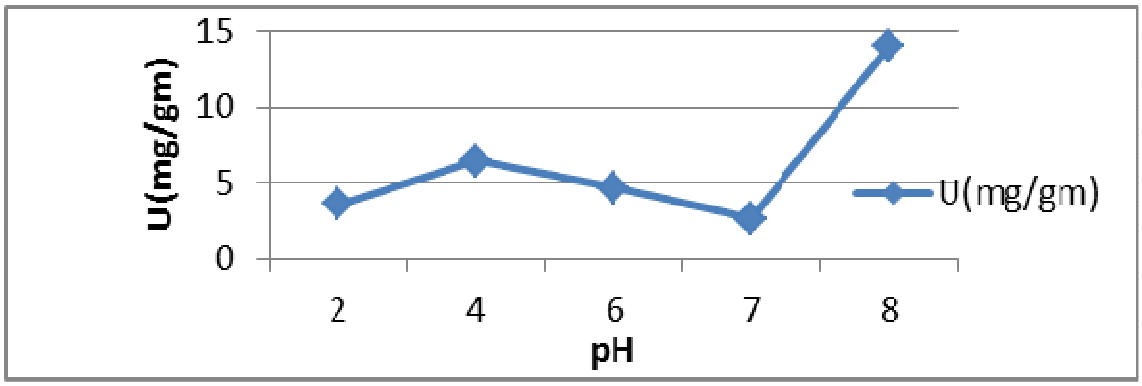
GRAPH 30

Pb(II) uptake by hydrogel 6vs pH



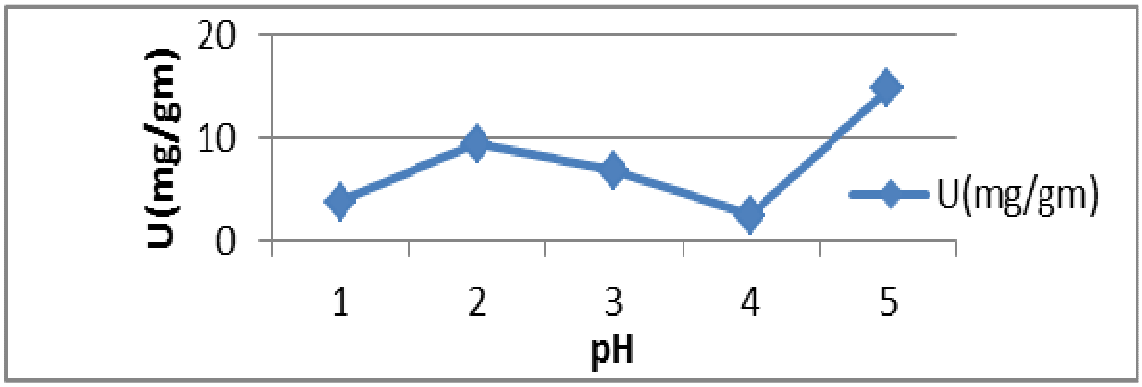
GRAPH 31

Cd(II) uptake by hydrogel 1vs pH



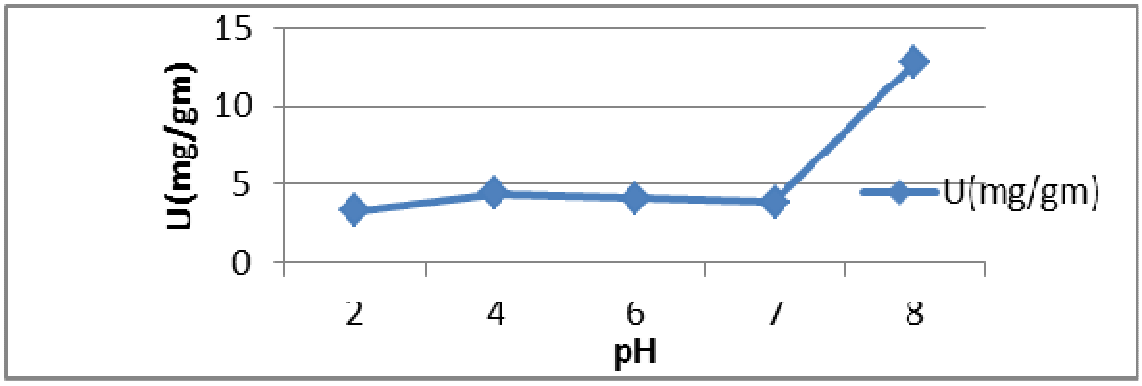
GRAPH 32

Cd(II) uptake by hydrogel 2vs pH



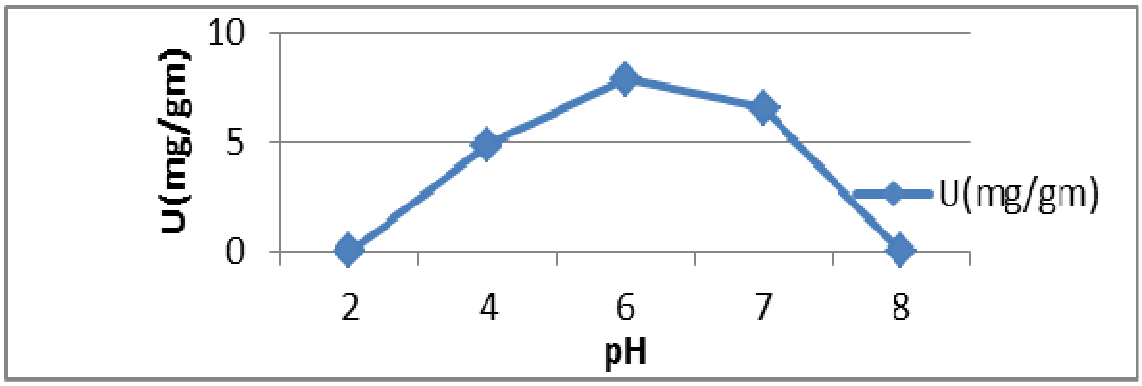
GRAPH 33

Cd(II) uptake by hydrogel 3vs pH



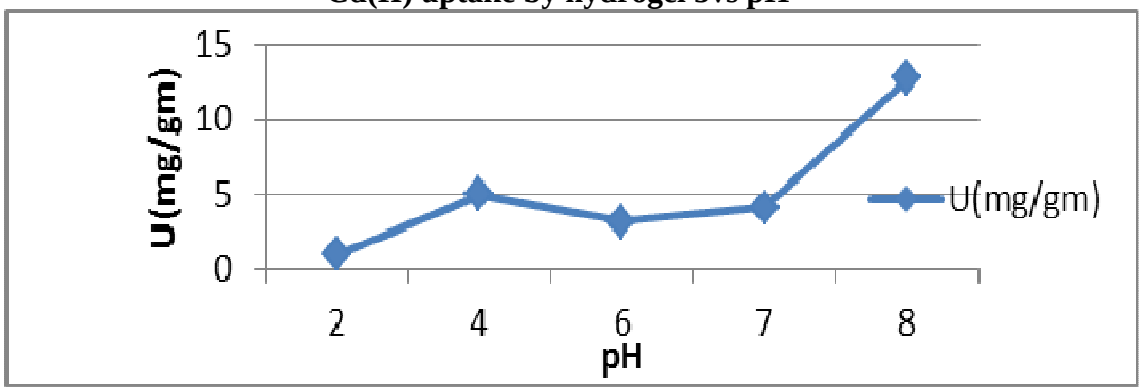
GRAPH 34

Cd(II) uptake by hydrogel 4vs pH



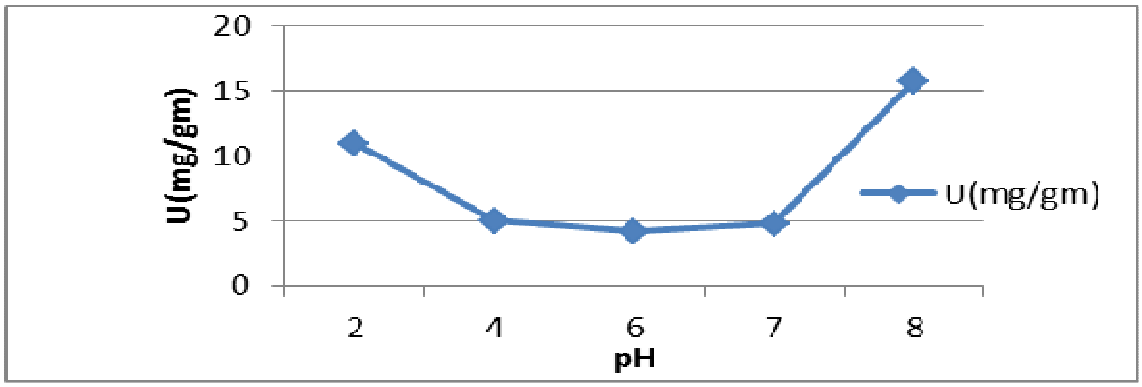
GRAPH 35

Cd(II) uptake by hydrogel 5vs pH



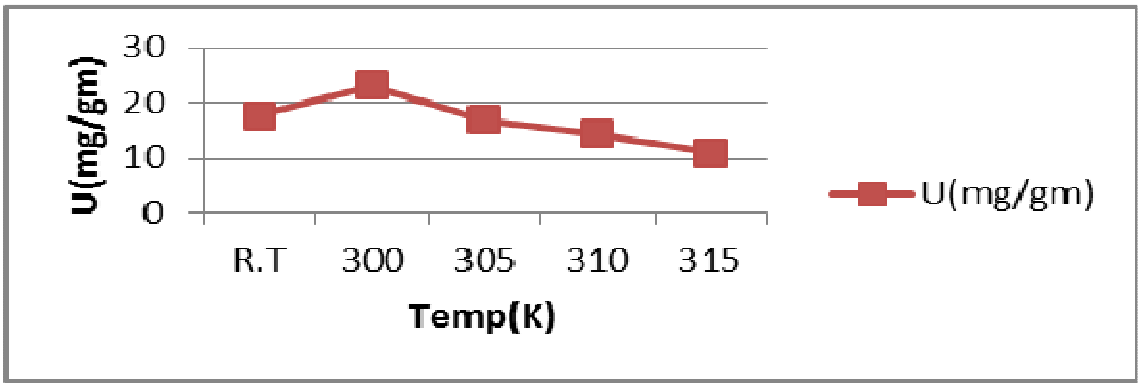
GRAPH 36

Cd(II) uptake by hydrogel 6vs pH



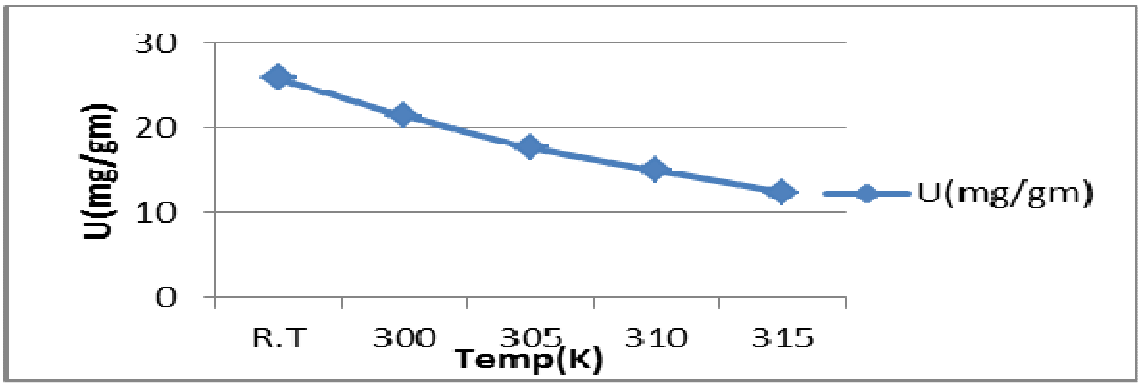
GRAPH 37

Hg(II) uptake by hydrogel 1vs TEMP



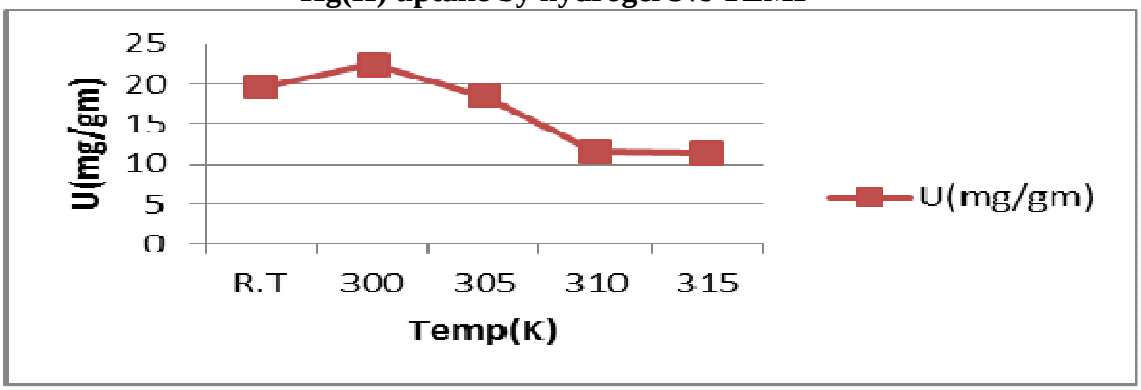
GRAPH 38

Hg(II) uptake by hydrogel 2vs TEMP



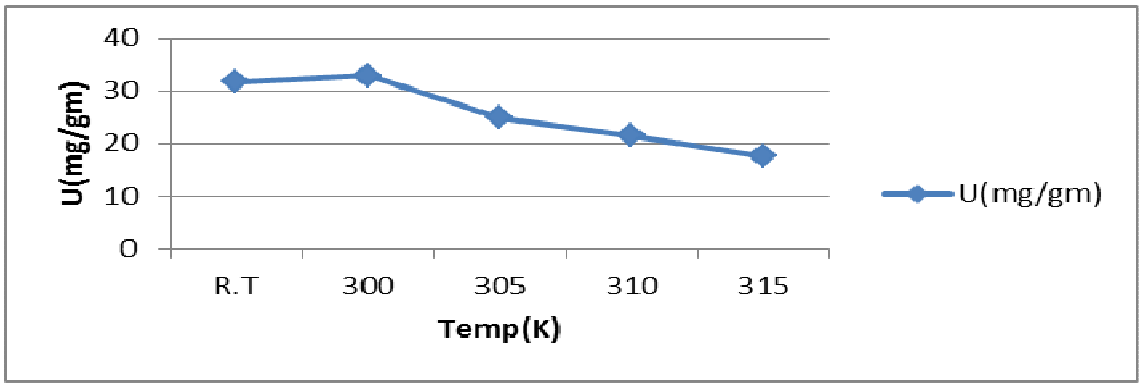
GRAPH 39

Hg(II) uptake by hydrogel 3vs TEMP



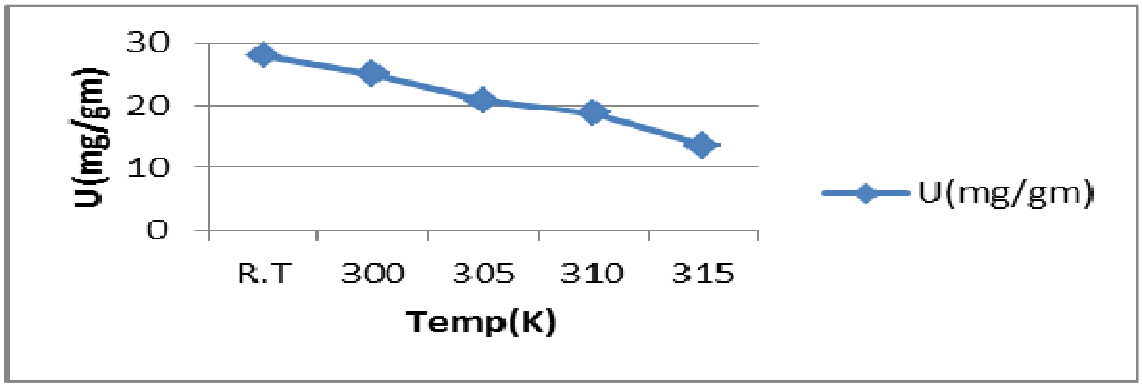
GRAPH 40

Hg(II) uptake by hydrogel 4vs TEMP



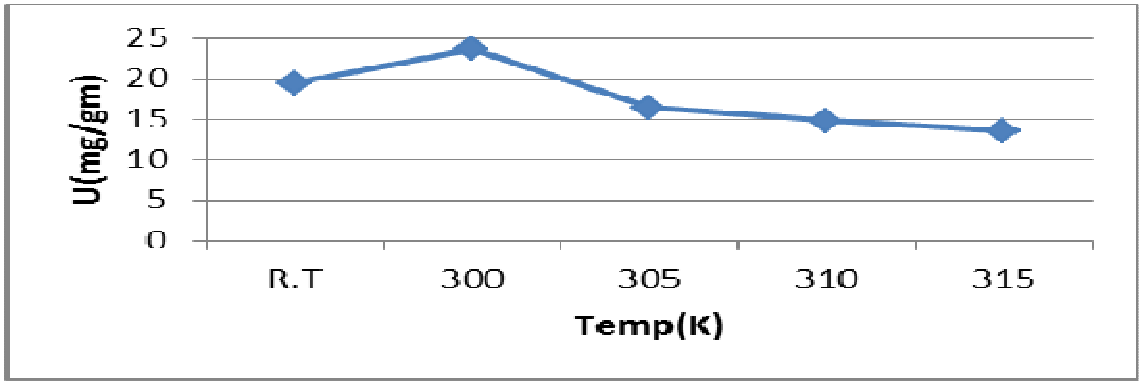
GRAPH 41

Hg(II) uptake by hydrogel 5vs TEMP

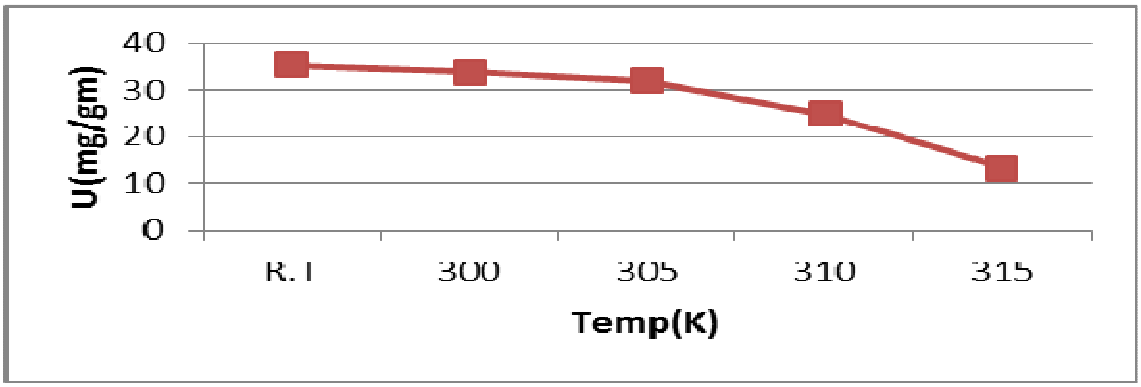


GRAPH 42

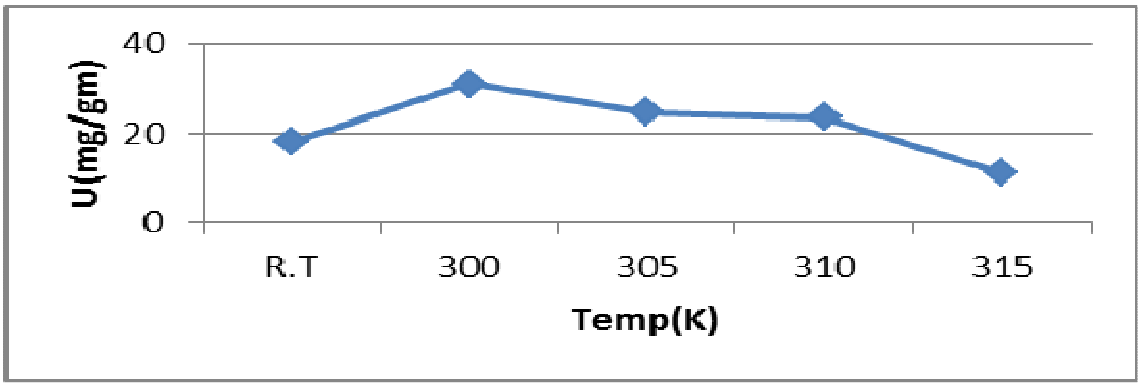
Hg(II) uptake by hydrogel 6vs TEMP



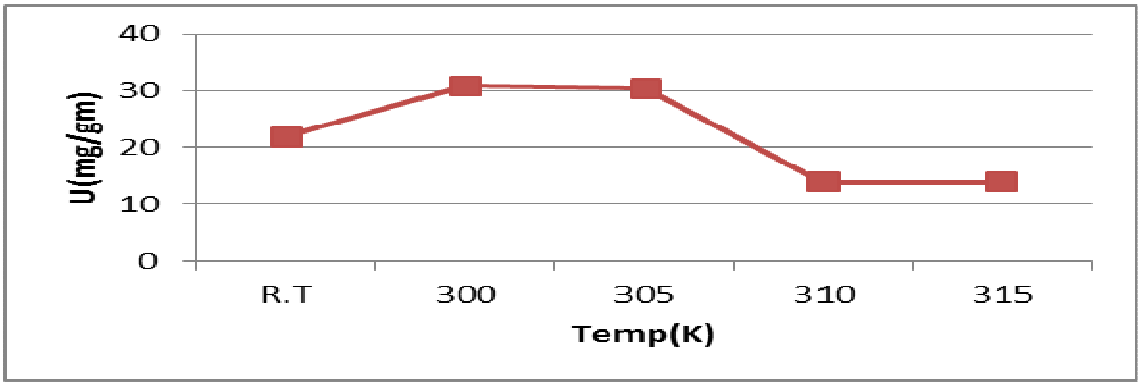
GRAPH 43
Pb(II) uptake by hydrogel 1vs TEMP



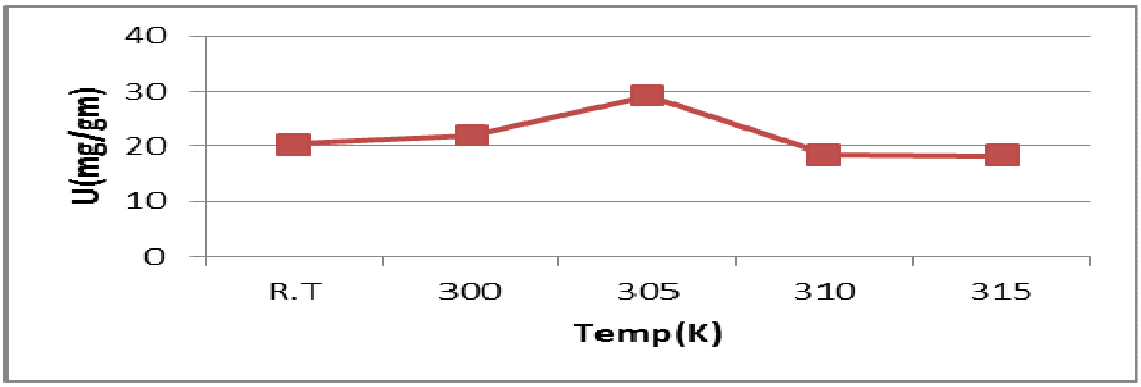
GRAPH 44
Pb(II) uptake by hydrogel 2vs TEMP



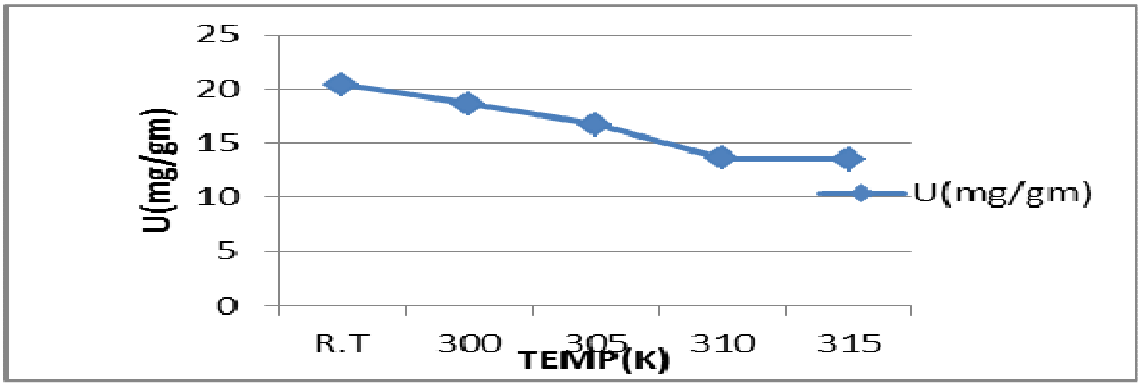
GRAPH 45
Pb(II) uptake by hydrogel 3vs TEMP



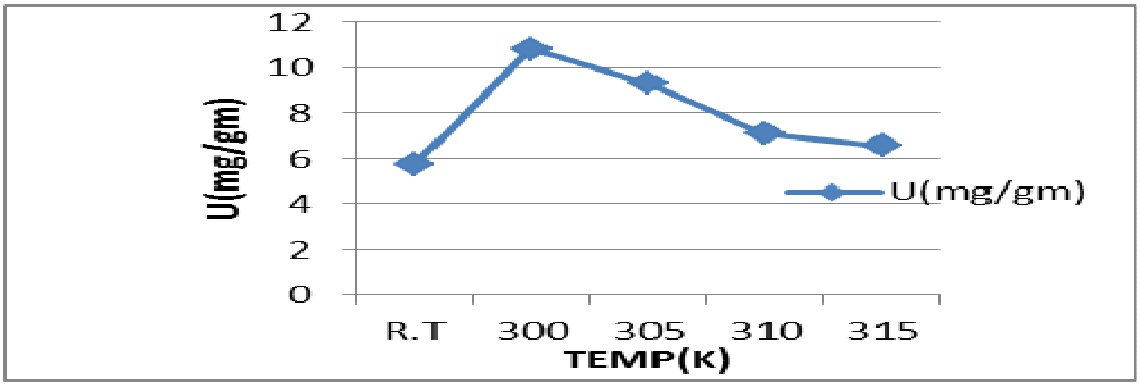
GRAPH 46
Pb(II) uptake by hydrogel 4vs TEMP



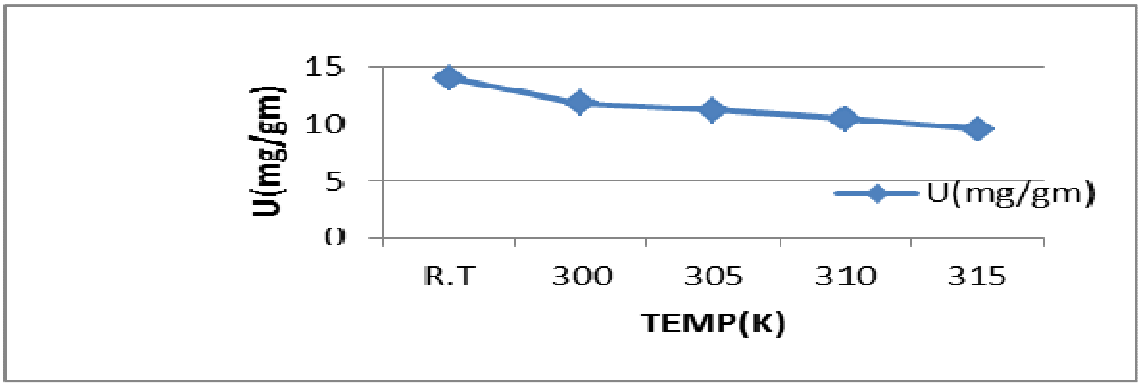
GRAPH 47
Pb(II) uptake by hydrogel 5vs TEMP



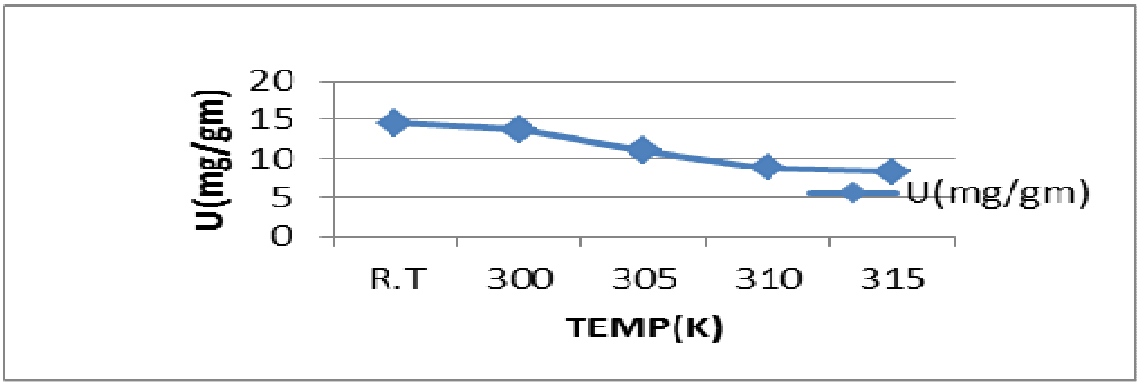
GRAPH 48
Pb(II) uptake by hydrogel 6vs TEMP



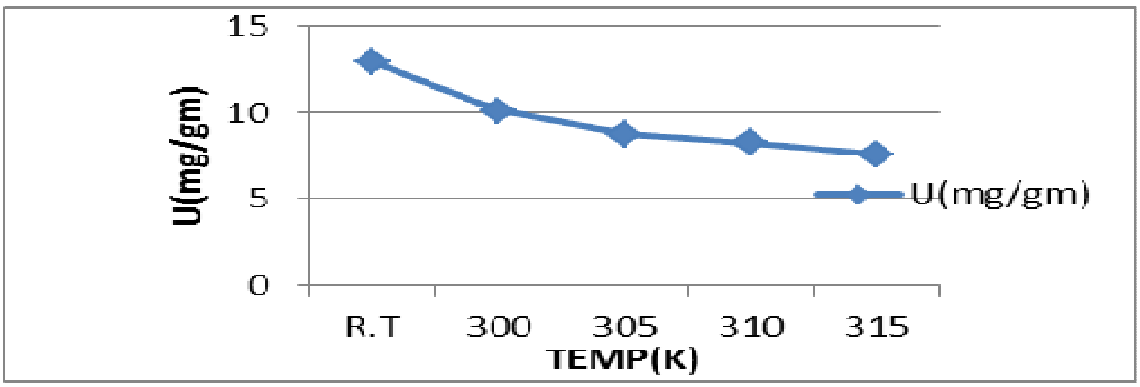
GRAPH 49
Cd(II) uptake by hydrogel 1vs TEMP



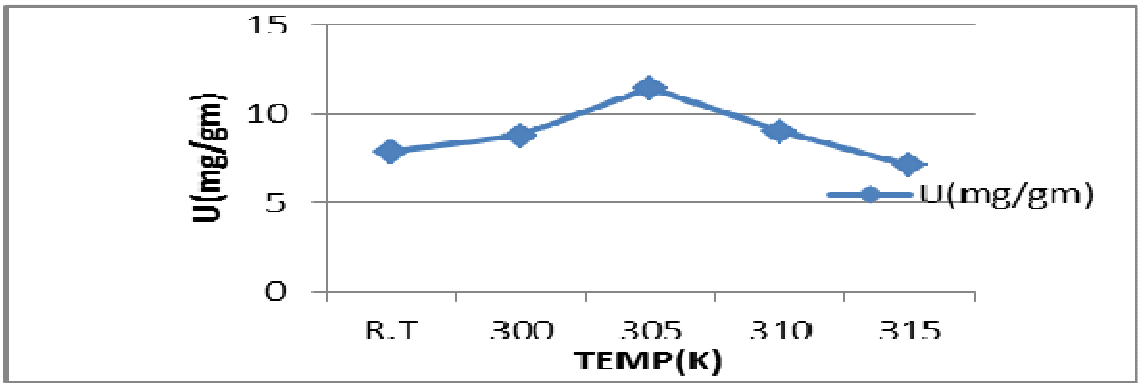
GRAPH 50
Cd(II) uptake by hydrogel 2vs TEMP



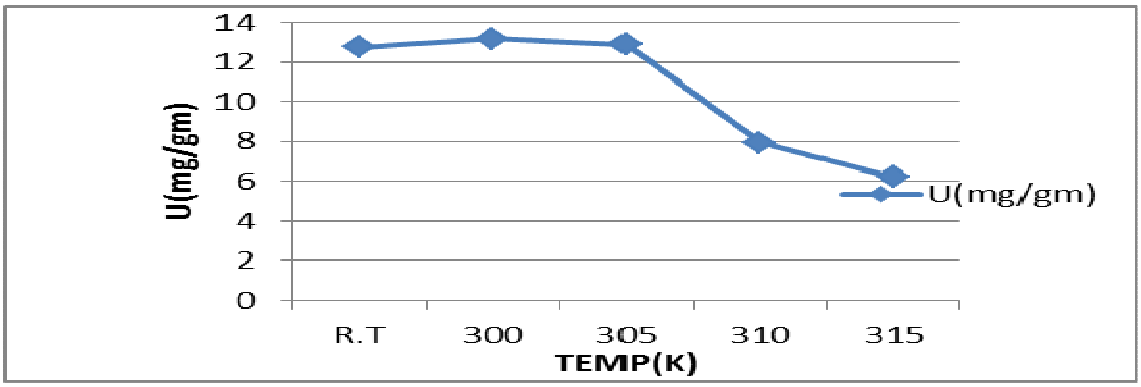
GRAPH 51
Cd(II) uptake by hydrogel 3vs TEMP



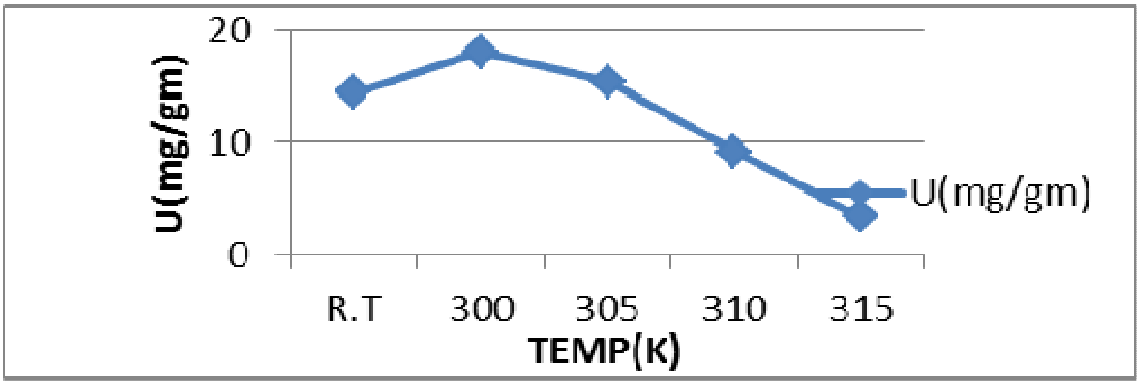
GRAPH 52
Cd(II) uptake by hydrogel 4vs TEMP



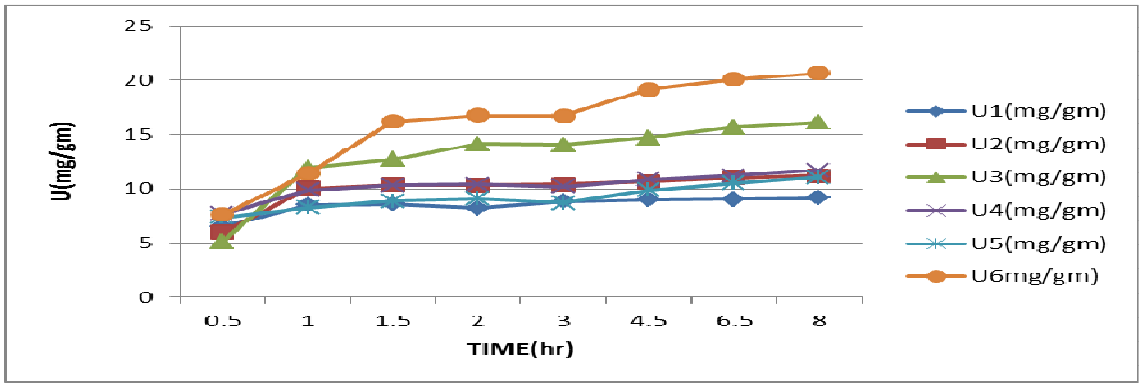
GRAPH 53
Cd(II) uptake by hydrogel 5vs TEMP



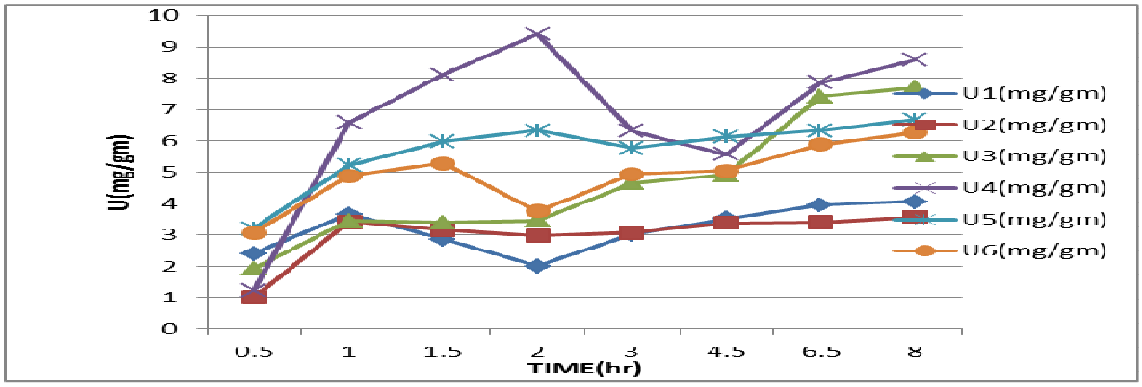
GRAPH 54
Cd(II) uptake by hydrogel 6vs TEMP



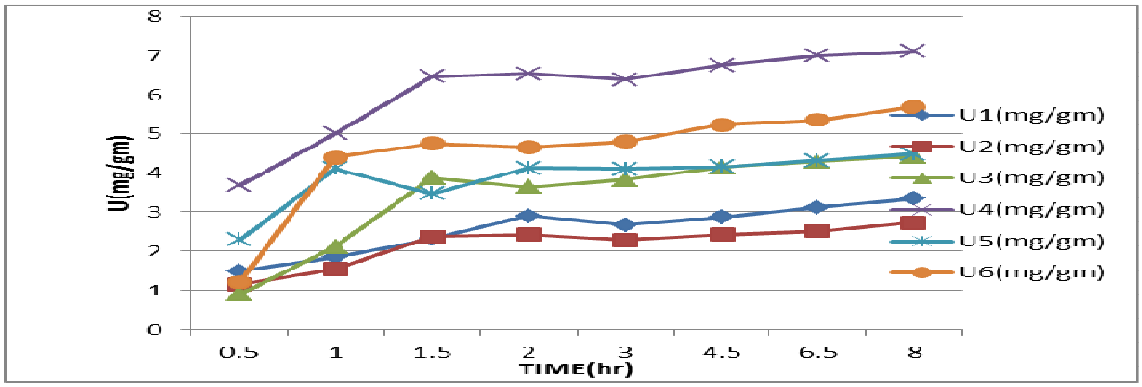
GRAPH 55
Hg(II) UPTAKE BY HYDROGEL vs TIME



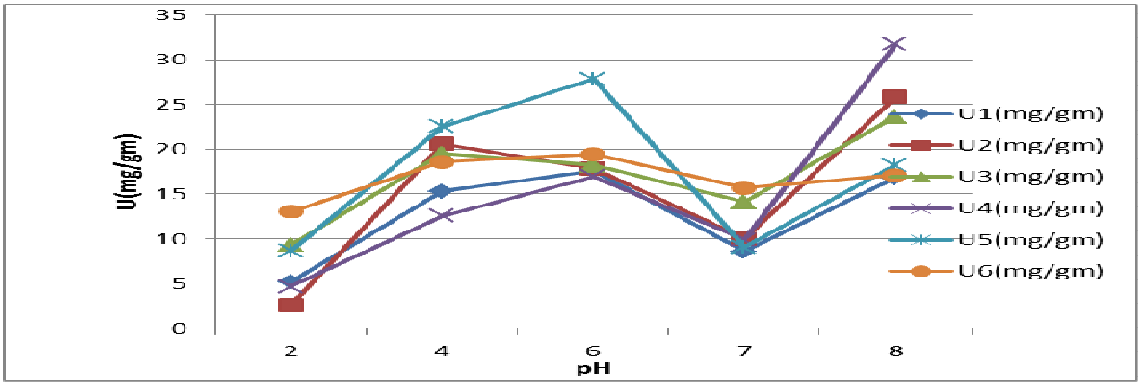
GRAPH 56
Pb(II) UPTAKE BY HYDROGEL vs TIME



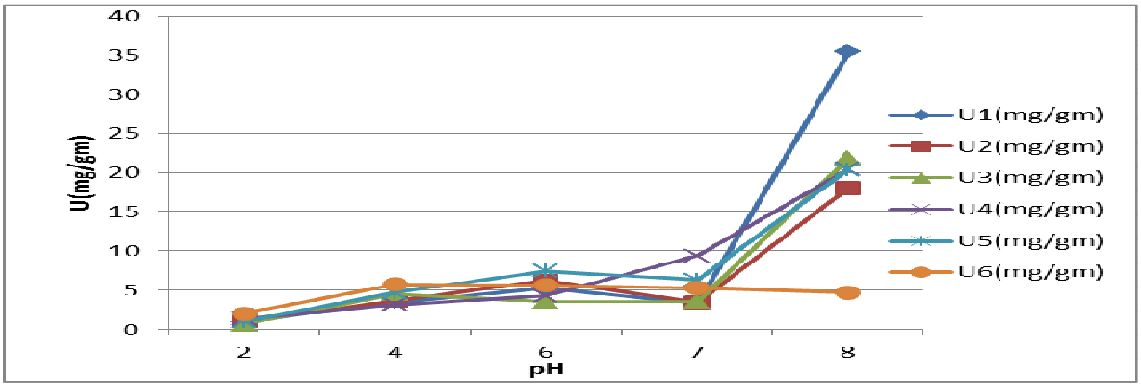
GRAPH 57
Cd(II) UPTAKE BY HYDROGEL vs TIME



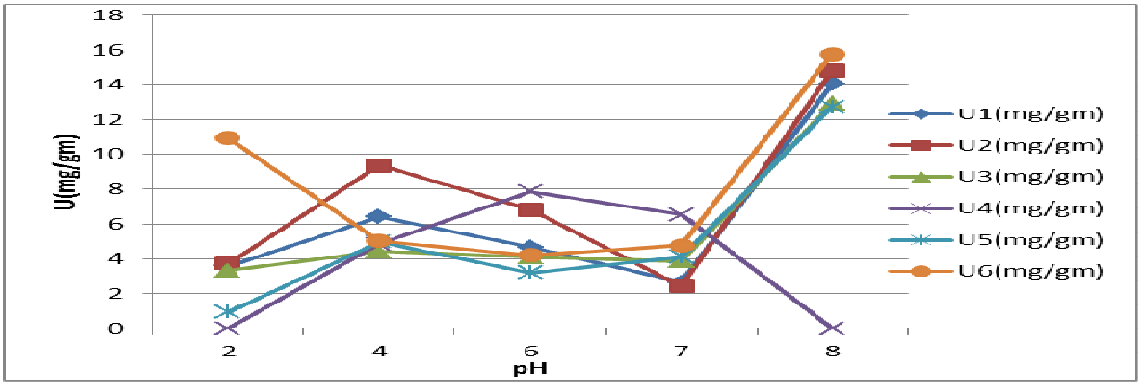
GRAPH 58
Hg(II) UPTAKE BY HYDROGEL vs pH



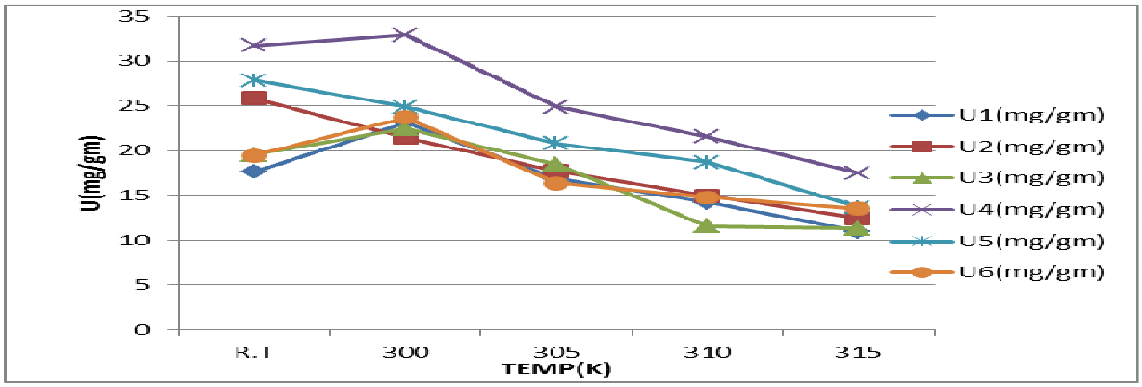
GRAPH 59
Pb(II) UPTAKE BY HYDROGEL vs pH



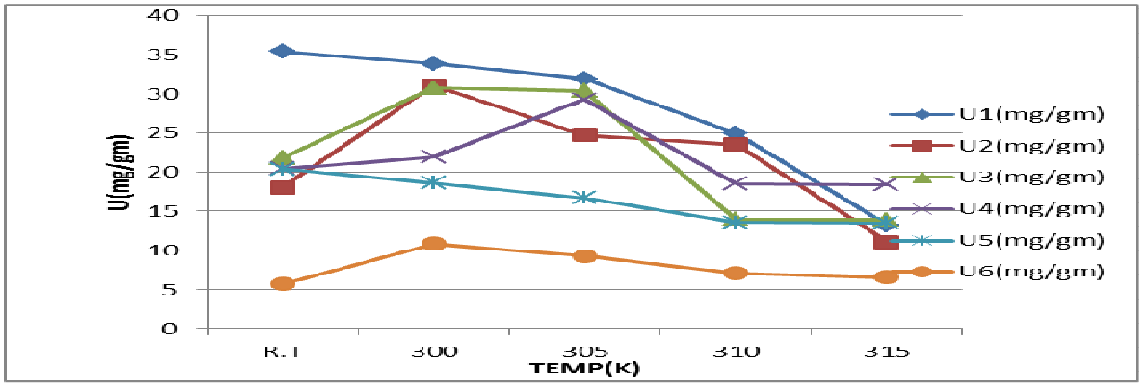
GRAPH 60
Cd(II) UPTAKE BY HYDROGEL vs pH



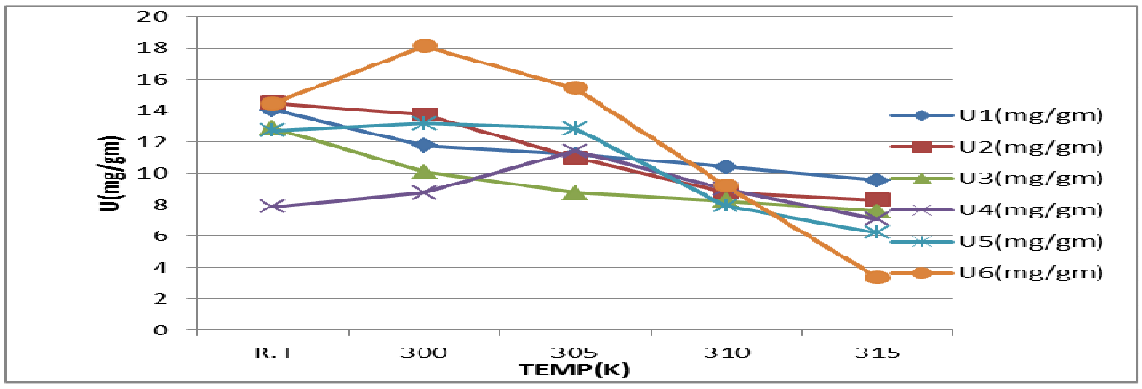
GRAPH 61
Hg(II) UPTAKE BY HYDROGEL vs TEMP



GRAPH 62
Pb(II) UPTAKE BY HYDROGEL vs TEMP



GRAPH 63
Cd(II) UPTAKE BY HYDROGEL vs TEMP



CONCLUSIONS

In the present work hydrogels of copolymers of Acrylamide with natural resources (Cane sugar juice , Sapodilla extract and Pine apple juice with the help of initiator KPS and crosslinker N,N-MBAAm were prepared .

Hydrogels were characterised by FTIR ,SEM ,and XRD .

FTIR gave information about various functional groups present in crosslinked network.

By SEM analysis surface morphology were found out.

With the help of XRD analysis is was found that materials are nearly amorphous in nature.

Swelling study of hydrogels were performed in aqueous media as function of time and it was found that nature of swelling is nearly same as that of fully synthetic material but extent were found different .

Swelling study also performed at different pH and temperature and it was found that hydrogels were responsive to these parameters to some extent.

Metal ion sorption study were also performed for Hg(II), Pb(II) and Cd(II) in aqueous media as a function of time and some fruitful results were obtained for these hydrogels . Sorption study were also performed as a function of pH and temperature and fruitful results were found.

It had been observed that for swelling study much better results can obtained if pellets size was taken as small as possible

For better results in the case of sorption study hydrogels must be finely powdered.

REFERENCES

1.1. Ferry, John D. Viscoelastic Properties of Polymers. New York: Wiley, 1980.

1.2. Terech P. Low-molecular weight organogelators. In: Robb ID, editor. Specialist surfactants. Glasgow: Blackie Academic and Professional, p. 208–268 (1997).

1.3.Van Esch J, Schoonbeek F, De Loos M, Veen EM, Kellog RM, Feringa BL. Low molecular weight gelators for organic solvents. In: Ungaro R, Dalcanale E, editors. Supramolecular science: where it is and where it is going. Kluwer Academic Publishers, p. 233–259 (1999).

1.4 .Kumar R, Katare OP. Lecithin organogels as a potential phospholipid-structured system for topical drug delivery: A review. American Association of Pharmaceutical Scientists PharmSciTech 6, E298–E310 (2005).

1.5. Carretti E, Dei L, Weiss RG. Soft matter and art conservation. Rheoreversible gels and beyond. Soft Matter 1, 17–22 (2005).

1.6 . Pernetti M, van Malssen KF, Flöter E, Bot A. Structuring of edible oil by alternatives to crystalline fat. Current Opinion in Colloid and Interface Science 12, 221–231 (2007).

1.7.Visintin RFG, Lapasin R, Vignati E, D'Antona P, Lockhart TP. Rheological behavior and structural interpretation of waxy crude oil gels. Langmuir 21, 6240–6249 (2005)

1.8. E.L. Cussler M.R.Stocker and J.E. Varferg, *AichEJ*,30,579(1984) .

1.9.Y.Oshada, "*Advances in Polymer science*" , Springer –Verlag, Berlin, 82, 1 (1987).

1.10.D.Shino, Y. Murata, K.Kataoka, Y. Koyama , T.Okano and Y. Sakuri, *Biomaterials*, 15,121,(1994).

1.11.R.Yoshida, Y. Kaneko , K. Sakai, T. Okano, Y.Sakurai and S.W.Kim, J.Contr.Release,32,97 (1994).

1.12.T.Aoki , M. Kawshima, H. Katono, K.Sanui, N.Ogata, T. Okano and Y.Sakurai , Macromolecules, 27,947, (1994) .

1.13.B.D. Ratner, in D.F. Williams , ed., *Biocompatibility Chemical Implant Materials*,CRC Press , Inc ., Boca Raton , Florida ,2,145(1981).

1.14.M.F.Refoju and M.Greyson , in Anthony Standen , ed., Kirk – Othmer "*Encyclopedia of Chemical Technology*"3rd edn ., 6, 720 , Jhon Wiley, NY (1979).

1.15.B.D.Ratner and A.S.Hoffman ,*ACS Symp.Ser*.,1,31(1976).

1.16.S.W.Kim,Peterson and J.Feijen ,in E.Ariens,ed., "*Drug Design* "10,193,Academic Press,NY(1980).

1.17.*bmew.ecn.purdue.edu/akkus/BIO2200.../Hydrogels.ppt - United States.*

1.18 .www.che.utexas.edu/research/biomat/PDFReprints/Ratner_Hydrogel

1.19 . M.Huglins,J.B.Yahya and M.B.Zakaria ,*Polymer*,23,340(1982).

1.20.O.Wichterle and D.Lim, *Nature*,185,117 (1960).

1.21.E.Setegency , G.Boyd and H.P.Gregor ,ed., 'Charged Gels and Membranes', Part I and II, D.Reidel Publishing Co.,Dordrecht,Holland (1976).

1.22.Drobnick , '*The Use of Polymer in Medicine (A Bibliography)*',Series Macro, B-1 Institute of Macromolecular Chemistry , Czechoslovak Academy of Sciences ,Prague (1977).

1.23 .M.F.Rafejo and H.S.Liu,*OphthSurg.*,9,43(1978).

1.24.M.Macret and G.Hild , *Polymer* ,23,748(1982).
1.25.J.Kolarik , *Adv .Polym.Sci.*,46,119 (1982).
1.25.1ocw.mit.edu/courses/chemical-engineering/10-467...fall.../4.pdf
1.26.Schild, H. G. "Poly(N-isopropylacrylamide): experiment, theory and application" *Progress in Polymer Science*, 1992, 17 (2), 163–249.
1.27.F. Haaf, A. Sanner and F. Straub (1985). "Polymers of N-Vinylpyrrolidone: Synthesis, Characterization and Uses". *Polymer Journal* 17 (1): 143–152. doi:10.1295/polymj.17.143
1.28. Fischer, Frank; Bauer, Stephan (2009). "Polyvinylpyrrolidon. Ein Tausendsassa in der Chemie". *Chemie in unserer Zeit* 43 (6): 376–383. doi:10.1002/ciuz.200900492
1.29.Bühler, Volker (2005). *Excipients for Pharmaceuticals - Povidone, Crospovidone and Copovidone*. Berlin, Heidelberg, New York: Springer. pp. 1–254. ISBN 978-3-540-23412.
1.30. Santhi Ganesan M.D Embolized Crospovidone (poly[N-vinyl-2-pyrrolidone]) in the Lungs of Intravenous Drug Users Mod Pathol 2003;16(4):286–292 [1]
1.31.PVP-Iodine Accessed January 25, 2007
1.32.Das SK, Saha SK, Das A, Halder AK, Banerjee SN, Chakraborty M (September 2008). "A study of comparison of efficacy and safety of talc and povidone iodine for pleurodesis of malignant pleural effusions". *Journal of the Indian Medical Association* 106 (9): 589–90, 592. PMID 19552086.
1.33. United States Patent 6730316
1.34.http://pubs.acs.org/doi/abs/10.1021/ol9001398
1.35.Dr. Stephan Bauer, Dr. Frank Fischer (2009). *Ein Polyvinylpyrrolidon (PVP): ein vielseitiges Spezialpolymer – Verwendung in der Keramik und als Metallabschreckmedium*. 61. pp. 382–385.
1.36.Göthlich, Alexander; Koltzenburg, Sebastian; Schornick, Gunnar (2005). "Funktionale Polymere im Alltag: Vielseitig". *Chemie in Unserer Zeit* 39 (4): 262–273. doi:10.1002/ciuz.200400346.
1.37.http://www.ispcorp.com/products/pharma/content/brochure/plasdonePovidone/PlasdonePovidone.pdf
1.38.Lillie RD & Fullmer HM (1976) Histopathologic Technic and Practical Histochemistry, 4th ed. New York: McGraw-Hill, p.411. ISBN 0070378622
1.39. (http://doc.utwente.nl/57855/1/thesis_Hiemstra.pdf) (from thesis of Hiemstra)
1.40.Hiroshi Inomata[a] and Shozaburo Saito[a] [a]Department of Molecular Chemistry and Engineering Faculty of Engineering, Tohoku University Aoba, Aramaki Aoba-ku, Sendai 980, JAPAN
1.41.Dibakar Dhara and Prabha R. Chatterji*(DOI: 10.1021/la980194k)
Speciality Polymers Group, Organic Coatings & Polymers Division, Indian Institute of Chemical Technology, Hyderabad 500 007, India Langmuir, 1999, 15 (4), pp 930, 935
1.42. VijayR. Tirumala[1] , Jan Ilavsky[1], and Michal Ilavsky[2]
[1]Advanced Photon Source, Argonne National Laboratories, Argonne, Illinois 60439
[2]Faculty of Mathematics and Physics, Charles University, 121 16 Prague, Czech Republic.
*1.43.T.Tanaka ,D.J . Fillmore ,S.T .Sun ,I.Nishio, G.Swisaglow and A.Shah,*Phys.Rev.Litt.,*45,1636(1980)*
1.44.M.Illavsky ,J.Hrouz , J.Stejskal and K.Bouchal ,Macromolecules ,*17,2868(1984).*
1.45.T.Tanaka, Sci.Am,*244,110(1981).*

1.46.T.Tanaka, Phys.Rev.Litt.,*40,820(1978).*
*1.47.N.Hirokawa and . T.Tanaka,*J .Chem.Phys., *81,6379(1985).*
*1.48.A.Katchalsky ,O.Kunjle and W.Kuhan,*J.Polym.Sci.,*5,283(1950).*
*1.49.A.Silburlerg, W.Kuhan,*Nature ,*170,450(1952).*
*1.50 .T.Tanaka ,L.O.Hocker and G.B.Benedek,*J.Chem,Phys.,*59 ,5151(1973).*
*1.51.J.P.Munch ,S.Candu,R.Duplessix,C.Picot,J.Herz and H.Benoit,*J.Polym.Sci, Polym Phys., *14,1097(1976).*
1.52.G.Patterson, 'International Symposium on Macromolecules' *Strasbourg ,France ,Abstract No .27(1981).*
*1.53.M.Adam and M.Delsanti,*J.Phys., 37,*1045(1976).*
1.54.R.Ullman,in J.E.Mark and J.Lal,ed., 'Elastomers and Rubber Elasticity'*,ACS,Washington.D.C., 257(1982).*
1.55.E.Geissler ,R. Duplessix and
*A. M.Hecht,*Macromolecules,*16,712(1983).*
1.56.P.Lutz, C.Picot,G.Hild and P.Rempp,Br.Polym.J.9,159(1983)
*1.57.A.M.Hecht and E.Giessler,*J.Chem,Phys.,*73,4077(1980).*
1.58.*T.Tanaka,S.Ishiwata and C.Ishimoto,*Phys.Rev.Litt.,*38, 711(1977).*
1.59.M.F.Refojo, ACS Symp.Ser.,31,37(1976).
1.60.Peppas, N.A., et al., *Hydrogels in pharmaceutical formulations.* European Journal of Pharmaceutics and Biopharmaceutics, 2000. 50(1): p. 27-46.
1.61.Fang, J.-Y., et al., *Transdermal iontophoresis of sodium nonivamide acetate: V. Combined effect of physical enhancement methods.* International Journal of Pharmaceutics, 2002. 235(1-2): p. 95-105.
1.62.Cohen, S., et al., *A novel in situ-forming ophthalmic drug delivery system from alginates undergoing gelation in the eye.* Journal of Controlled Release, 1997. 44(2 3): p. 201-208.

1.63.N.A. Peppas: Hydrogels in Medicine and Pharmacy, Vol. 1. Fundamentals, CRC Press, Boca Raton, FL, 1986, 180 pages.
1.64.Simonsen, L., et al., *Dextran hydrogels for colon-specific drug delivery. V. Degradation in human intestinal incubation models.* European Journal of Pharmaceutical Sciences, 1995. 3(6): p. 329-337.
1.65.George, M. and T.E. Abraham, *pH sensitive alginate-guar gum hydrogel for the controlled delivery of protein drugs.* International Journal of Pharmaceutics, 2007. 335(1-2): p. 123-129.
1.66.Kim, B. and N.A. Peppas, *In vitro release behavior and stability of insulin in complexation hydrogels as oral drug delivery carriers.* International Journal of Pharmaceutics, 2003. 266(1-2): p. 29-37.
1.67.Ryu, J.-M., et al., *Increased bioavailability of propranolol in rats by retaining thermally gelling liquid suppositories in the rectum.* Journal of Controlled Release, 1999. 59(2): p. 163-172.
1.68.Miyazaki, S., et al., *Thermally reversible xyloglucan gels as vehicles for rectal drug delivery.* Journal of Controlled Release, 1998. 56(1-3): p. 75-83.
1.69. Sun, Y.-M., et al., *Composite poly(2-hydroxyethyl methacrylate) membranes as ratecontrolling barriers for transdermal applications.* Biomaterials, 1997. 18(7): p. 527-533.

1.70.Gayet, J.C. and G. Fortier, *High water content BSA-PEG hydrogel for controlled release device: Evaluation of the drug release properties.* Journal of Controlled Release, 1996. 38(2-3): p. 177-184.
1.71.Hubbell, J.A., *Hydrogel systems for barriers and local drug delivery in the control of wound healing.* Journal of Controlled Release, 1996. 39(2-3): p. 305-313.
1.72.Park, H. and K. Park, *Biocompatibility Issues of Implantable Drug Delivery Systems.* Pharmaceutical Research, 1996. 13(12): p. 1770-1776.
1.73.Fibrin Sealants - test, blood, complications, time, infection, risk, rate, Definition, Purpose, Description, Preparation, Normal results
1.74.Atrah HI (April 1994). "Fibrin glue". *BMJ* 308 (6934): 933–4.PMC 2539755. PMID 8173397.
1.75.Evans LA, Ferguson KH, Foley JP, Rozanski TA, Morey AF (April 2003). "Fibrin sealant for the management of genitourinary injuries, fistulas and surgical complications". *The Journal of Urology* 169 (4): 1360–2. doi:10.1097/01.ju.0000052663.84060.ea. PMID 12629361.
1.76.Feinstein AJ, Varela JE, Cohn SM, Compton RP, McKenney MG (2001). "Fibrin glue eliminates the need for packing after complex liver injuries". *The Yale Journal of Biology and Medicine* 74 (5): 315–21. PMC 2588746. PMID 11769337.
1.77. Bastarache JA (March 2009). "The complex role of fibrin in acute lung injury". *American Journal of Physiology. Lung Cellular and Molecular Physiology* 296 (3): L275–6. doi:10.1152/ajplung.90633.2008. PMID 19118088.
1.78.Modi P, Rahamim J (July 2005). "Fibrin sealant treatment of splenic injuries during oesophagectomy". *European Journal of Cardio-thoracic Surgery* 28 (1): 167–7. doi:10.1016/j.ejcts.2005.02.045. PMID 15876541.
1.79.Patel R, Caruso RP, Taneja S, Stifelman M (November 2003). "Use of fibrin glue and gelfoam to repair collecting system injuries in a porcine model: implications for the technique of laparoscopic partial nephrectomy". *Journal of Endourology* 17 (9): 799–804. doi:10.1089/089277903770802416. PMID 14642047.
1.80.Toda K, Yoshitatsu M, Izutani H, Ihara K (August 2007). "Surgical management of penetrating cardiac injuries using a fibrin glue sheet". *Interactive Cardiovascular and Thoracic Surgery* 6 (4): 577–8. doi:10.1510/icvts.2007.156372. PMID 17669945.
1.81."AME: Heart Valves". www.ame.hia.rwth-aachen.de. Retrieved 2010-05-31.
1.82."AME: Vascular Grafts". www.ame.hia.rwth-aachen.de. Retrieved 2010-05-31.
1.83. ibid,WIKIPEDIA
1.84.G.A.Urban and T.Wiess.,*Hydrogel for Biosensors.*
1.85.Andreou, V.G. and Y.D. Clonis, A portable fiber-optic pesticide biosensor based on immobilized cholinesterase and sol-gel entrapped bromcresol purple for in-field use. Biosensors & Bioelectronics, 2002. 17(1-2): p. 61-69.
1.86.Doong, R.A. and H.C. Tsai, Immobilization and characterization of sol-gel-encapsulated acetylcholinesterase fiber-optic biosensor. Analytica Chimica Acta, 2001. 434(2): p. 239-246.
1.87.Fine, T., et al., Luminescent yeast cells entrapped in hydrogels for estrogenic endocrine disrupting chemical biodetection. Biosens Bioelectron, 2006. 21(12): p. 2263-9.

1.88.Ivask, A., et al., Fibre-optic bacterial biosensors and their application for the analysis of bioavailable Hg and As in soils and sediments from Aznalcollar mining area in Spain. Biosens Bioelectron, 2007. 22(7): p. 1396-402.
1.89.Department of Chemical and Biomolecular Engineering, Yonsei University .,Republic of Korea
1.90.Stéphanie Pasche, Réal Ischer, Guy Voirin, Martha Liley, Jean Luprano , *CSEM SA, Neuchâtel, Switzerland* .
1.91. Analytical Biochemistry (2009) Volume: 392, Issue: 1, Publisher: Elsevier Inc., Pages: 1-7
1.92.Jun Yan,[1] Valber A. Pedrosa,[2] Aleksandr L. Simonian,[2] and Alexander Revzin[1*]
[1]Department of Biomedical Engineering, University of California, Davis, 451 East Health Sciences St. #2619, Davis, CA 95616, USA
[2]Departments of Materials Engineering, Auburn University, Auburn, AL 36849, USA.
1.93.www.ncbi.nlm.nih.gov/pubmed/19625066.
1.94.psrt.cusat.ac.in/apt10/apt10CD/HTMLS/ORAL/CMP12N.%20Narayanan%20Reddy.pdf
1.95.Erdener Karadağ[1,*], Ömer Barış Üzüm[1], Semiha Kundakci[1], Dursun Saraydin[2] Article first published online: 22 JAN 2007 DOI: 10.1002/app.25397
1.96.http://www.iwtc.info/2006_pdf/02-5.pdf
1.97.http://www.gnest.org/journal/Vol12_no3/262-269_720_Bekiari_12-3.pdf
1.98. DOI: 10.1002/pat.1554 (Ece Kök Yetimoğlu, Melike Fırlak, Memet Vezir Kahraman, Sabahattin Deniz)

2.1. Malcolm B. Huglin, M.B.Z., *Swelling properties of copolymeric hydrogels prepared by gamma irradiation*. 1986. p. 457-475
2.2. Sperinde, J.J. and L.G. Griffith, *Control and Prediction of Gelation Kinetics in Enzymatically Cross-Linked Poly(ethylene glycol) Hydrogels*. 2000. p. 5476-5480.
2.3. Takamura, A., F. Ishii, and H. Hidaka, *Drug release from poly(vinyl alcohol) gel prepared by freeze-thaw procedure.* Journal of Controlled Release, 1992. 20(1): p. 21-27.
2.4. Eagland, D., N.J. Crowther, and C.J. Butler, *Complexation between polyoxyethylene and polymethacrylic acid--the importance of the molar mass of polyoxyethylene.* European Polymer Journal, 1994. 30(7): p. 767-773.
2.5. Gayet, J.C. and G. Fortier, *High water content BSA-PEG hydrogel for controlled release device: Evaluation of the drug release properties.* Journal of Controlled Release, 1996. 38(2-3): p. 177-184.
2.6. Hubbell, J.A., *Hydrogel systems for barriers and local drug delivery in the control of wound healing.* Journal of Controlled Release, 1996. 39(2-3): p. 305-313.
2.7. Peppas, N.A. and J.J. Sahlin, *Hydrogels as mucoadhesive and bioadhesive materials: a review*. Biomaterials, 1996. 17(16): p. 1553-1561.

2.8: Sugar Milling Research Institute, University of Natal, King George V Avenue, Durban, 4001
2.9. http://www.sugarindia.com/sugarcanetable.htm
2.10. http://docsdrive.com/pdfs/medwelljournals/jftech/2005/326-330.pdf
2.11. http://foodscience.wikispaces.com/Pineapple

3.1.References Griffiths, P.; de Hasseth, J.A. (18 May 2007). *Fourier Transform Infrared Spectrometry* (2nd ed.). Wiley-Blackwell. ISBN 0471194042.
3.2."The Infracord double-beam spectrophotometer". *Clinical Science* 16 (2). 1957.
3.3. Knoll, Max (1935). "Aufladepotentiel und Sekundäremission elektronenbestrahlter Körper". *Zeitschrift für technische Physik* 16: 467–475.
3.4. Suzuki, E. (2002). "High-resolution scanning electron microscopy of immunogold-labelled cells by the use of thin plasma coating of osmium". *Journal of Microscopy* 208 (3): 153–157. doi:10.1046/j.1365-2818.2002.01082.x.
3.5.Seligman, Arnold M.; Wasserkrug, Hannah L.; Hanker, Jacob S. (1966). "A new staining method for enhancing contrast of lipid-containing membranes and droplets in osmium tetroxide-fixed tissue with osmiophilic thiocarbohydrazide (TCH)". *Journal of Cell Biology* 30 (2): 424–432. doi:10.1083/jcb.30.2.424. PMC 2106998. PMID 4165523.
3.6. Malick, Linda E.; Wilson, Richard B.; Stetson, David (1975). "Modified Thiocarbohydrazide Procedure for Scanning Electron Microscopy: Routine use for Normal, Pathological, or Experimental Tissues". *Biotechnic and Histochemistry* 50 (4): 265–269. doi:10.3109/10520297509117069.
3.7. Wergin, W. P.; Erbe, E. F. (1994). "Snow crystals: capturing snow flakes for observation with the low-temperature scanning electron microscope". *Scanning* 16 (Suppl. IV): IV88.
3.8. Barnes, P. R. F.; Mulvaney, R.; Wolff, E. W.; Robinson, K. A. (2002). "A technique for the examination of polar ice using the scanning electron microscope". *Journal of Microscopy* 205 (2): 118–124. doi:10.1046/j.0022-2720.2001.00981.x. PMID 11879426.
3.9. Hindmarsh, J. P.; Russell, A. B.; Chen, X. D. (2007). "Fundamentals of the spray freezing of foods—microstructure of frozen droplets". *Journal of Food Engineering* 78 (1): 136–150. doi:10.1016/j.jfoodeng.2005.09.011.
3.10. http://en.wikipedia.org/wiki/Scanning_electron_microscope.
3.10(A) http://www.hhtc.ca/microscopes/sem/s3700N.htm
11.wikipedia

3.12.http://www.mf.mpg.de/de/abteilungen/mittemeijer/english/commentary/Powder%20Diffraction%20in%20Mat.Sci.pdf
3.13. http://epswww.unm.edu/xrd/xrdbasics.pdf
3.14. http://mams.rmit.edu.au/n4mrn7zr21d31.jpg
3.15.GOOGLE IMAGE.
3.16. pubs.acs.org/doi/abs/10.1021/jp104890c
3.17. linkinghub.elsevier.com/retrieve/pii/S0039602801019641

4.1.B.T.Po,K.Adachi and T. Kotaka , *Macromolecules*,20,2563(1987).
4.2.*ibid*.2569 (1987).
4.3. *ibid*.2574 (1987).
4.4.J.D.Andrade,ed., "*Hydrogel for Medical and Related Applications*", ACS Symposium Series,31,Acs,WashingtonD.C.(1976).
4.5.J.B.Anderson,ed., "*Biomaterials84*",Transactions,Second World Congress of Biomaterials,7,Washington,D.C.(1984).
4.6.J Janacek ,A Stoy and V.Stoy ,J.Polym.Sci., Polym. Symp., 53,299(1974).

4.7.Y.Ikada ,*High Swelling Gels* ,in J.Kahoveri, ed ., *Macromol Symp.36th Microsymposium on Macromol.*,Hinting and Wepf Verlag . Zag., Switzerland (1995).
4.8.R.L.Whistler, Tappi, 60 ,64,(1977).
4.9.B.D.Ratner and A.S.Hoffman in J.D. Andrade , ed ., "*Hydrogel for Medical and Related Applications*", ACS Symposium Series,31,Acs,WashingtonD.C.(1976).
4.10.T.Tanaka , D. Fillmore, S. T. Sin ,I. Nishio , G.Swislow and A.Snah , *Phys . Rev.Lett.*,45,1636(1980).
4.11.T.Tanaka,*Sci.Am* .,224, 124 , (1981).
4.12. T.Tanaka I. Nishio ,S.T. Sin S.Veno-Nishio, *Science* , 218 ,467 (1982).
4.13. Y .Hirokawa and T.Tanaka , *J.Chem .Phys* ., 31,6369 (1981) .
4.14. A.S .Hoffman , A.Affrassiabi and L.C .Dong ,in " *Reversible Swelling and Deswelling of Hydrogels",* Paper presented at ACS meeting ,NY(1986).
4.15.T.Tanaka , in "Critical Dyanamics, Kinetics and Phase Transitions Of Polymer Gels", Paper presented at ACS meeting ,NY(1986).
4.16.C.K.Chiklis and J.M.Grasshoff , J.Polym .Sci., A,2, 8,1617(1970).
4.17.L.D.Taylor and L.D. Cerankowski, *J.Polym.Sci Polym .Chem* ., 13 ,2551(1975).
4.18.T.Okano,Y.H.Bae and S.W.Kim , in "*Insulin Permeation Through Temperature Sensitive Hydrogels "*, Paper presented at ACS meeting ,NY(1986).
4.19. A.S .Hoffman , A.Affrassiabi and L.C .Dong, "*Delivery and Removal of Substances to and from Surrounding Solutions Using Thermally Reversible Gels"*,Paper presented at IUPAC Conference , Macromolecules86, Oxford , England (1986).
4.20.J.N.Hamid and O.Oguz , J.*Appl.Polym.Sci*., 60,971(1978)
4.21.J.Eliasaff , *J .Appl.Polym.Sci*.,22,873(1978).
4.22.I.D.Robb, in C.A.Finch ,ed., *'Chemistry and Technology of Water Soluble Polymers'* , Plenum,NY(1983).
4.23.B.D.Ratner, in J.L.Aggrawal, ed., *'Comprehensive Polymer Science'* ,Pergamon,Oxford,U.K., 201(1989)
4.24(a).(.Http://Www.Che.Utexas.Edu/Research/Biomat/Pdfreprints/Ratner_Hydrogels)
4.24. O .Hirisa, S.Ito, Y. Yamauchi, S.Fujashige & H.Ichigo, In D. De Rossi, ' Polymer Gels', Plenum, Ny, 247(1991)
4.25. B.G.Kalra And S.H.Gehrke, Polym. Commun.,32,322(1911)
4.26. H.S.Wu, A.S. Hoffman And P.Yager, J. Polym. Sci., Part A, 30,2121
4.27. P.De Boer And A.J.Pennwas, J.Polym.Phy., 14,187 (1987)
4.28. N.Wada Y. Kajima, Y.Yagi, H.Inomata And S.Saito, Langmuir,9,1(1993).
4.29. H.Inomata, S.Gota And S.Saito, Macromolecules, 23,4887(1990).
4.30. T.V.Budtora, N.G.Belnikevich, I.E. Snleiminor and S.Y. Frankiel, *Polymer*, 34,5154(1993).
4.31. Y. Osada, *Adv. Polym. Sci., Polym. Phys,* ed., 82.1 (1987).
4.32. T.Tanaka, I.Nishio, S.T.Sun, S. Veno-Nishio, Science,218, 467 (1982).
4.33. Lin, C.-C. and A.T. Metters, *Hydrogels in controlled release formulations: Network design and mathematical modeling.* Advanced Drug Delivery Reviews, 2006. 58(12-13) p. 1379-1408.
4.34. Paul J. Flory, N.R.M.C.S., *Dependence of elastic properties of vulcanized rubber on the degree of cross linking*. 1949. p. 225-245.
4.35. Turner, A., Jr., *The physics of rubber elasticity. L. R. G. Treloar, Oxford Univ. Press, New York, 1949, 262 pp.* 1950. p. 387.

4.36. Nikolaos A. Peppas, E.W.M., *Crosslinked poly(vinyl alcohol) hydrogels as swollen elastic networks*. 1977. p. 1763-1770.
4.37.K.Otake , H.Inomata,M.Kono and S.Saito, *J.Chem.Phys*.,91,1345(1989)
4.38.M.Marchetti,S.Pragev and E.L.Cuester ,*Macromolecules*,23,1760(1990)
4.39.*ibid*., 23,3445(1990)
4.40.A.K.Lele,M.V.Badiger,M.M.Hirve and R.A.Mashellkar,*Chem.Eng.Sci*., 50.3535(195)
4.41.M.M.Prange,H.H.Hooper and J.M.Prausnitz,*ALChE,J.*,35,803(1989)
4.42. http://pdf.lookchem.com/pdf/20/kim-30-5-7-0602-3.pdf

5.1.H.S.Buyn , R.P.Burford and A.G.Fane , *J.Appl.Polym .Sci*.,52,825(1994).

5.2.J.Jegal and Kew-HoLee,*J.Appl.Polym.Sci*.,60,1177(1996).

5.3.K.N.Bakeev ,E.A.Ponomartenko,T.V.Shiskanova,D.A.Tirell,A.B.Zezin and V.A.Kabanov,*Macromolecules* ,28,2886(1995).

5.4: Ghanshyam S. Chauhan, Anita Kumari, Rakesh Sharma (24 JUL 2007) (DOI: 10.1002/app.26729)
5.5: Ghanshyam S. Chauhan, Baljit Singh, Sandeep Chauhan, Monica Verma and Swati Mahajan ;Department of Chemistry, Himachal Pradesh University, Shimla - 17005,India(17October2005).
http://www.sciencedirect.com/science/article/pii/S0011916405003929
5.6: Nadia G. Kandile and Abir S. Nasr ; Chemistry Department, Faculty of Women, Ain Shams University, Heliopolis 11757, Cairo, Egypt(9 February 2011).(doi:10.1016/j.carbpol.2011.02.004)
5.7: G. Roshan Deen ; Natural Science and Science Education (NSSE), National Institute of Education, Nanyang Technological University, Singapore
http://www.tandfonline.com/doi/pdf/10.1080/01932690903297207
5.8:http://www.ncsu.edu/bioresources/BioRes_03/BioRes_03_1_0046_Nada_AF_SynthChar_GraftedCellulose_Metal.pdf
5.9: http://www.akamaiuniversity.us/PJST11_2_488.pdf
5.10: http://www.sciencedirect.com/science/article/pii/S0011916401850098
5.11: http://www.sciencedirect.com/science/article/pii/S1381514807000399
5.12: http://www.scientific.net/MSF.609.255
5.13. http://www.springerlink.com/content/w37578551w6751n2/
5.14. http://www.sciencedirect.com/science/article/pii/S0969806X08002235
5.15. http://www.sciencedirect.com/science/article/pii/S0301479707001892