Ph.D. Thesis

Synthesis and Applications of Polymeric Hydrogels as Heavy Metal Ions and other Industrially Important Metal Ion Sensor

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Dedicated

To

My Family

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DECLARATION

I hereby declare that the thesis entitled "**Synthesis and Applications of Polymeric Hydrogels as Heavy Metal Ions and other Industrially Important Metal Ion Sensor**" is an original work carried out by me under the supervision of **Prof. Sudhir G. Warkar and Prof. Anil Kumar**, Department of Applied Chemistry, Delhi Technological University, Delhi. This thesis has been prepared in conformity with the rules and regulations of the Delhi Technological University, Delhi. The research work reported and results presented in the thesis have neither partially nor fully submitted to any other university nor institute for the award of any other degree or diploma.

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CERTIFICATE

This is to certify that the work embodied in the thesis entitled "**Synthesis and Applications of Polymeric Hydrogels as Heavy Metal Ions and other Industrially Important Metal Ion Sensor**" by **Ms. Deepti Chauhan (Roll No 2K18/PhD/AC/05),** in the partial fulfilment of the requirements for the award of the degree of **Doctor of Philosophy**, is an authentic record of student's own work carried out by her under the supervision of **Prof. Sudhir G. Warkar and Prof. Anil Kumar** Faculties of Department of Applied Chemistry, Delhi Technological University, Delhi.

This is also certified that this work has neither partially nor fully submitted to any other Institute or University for the award of any other diploma or degree.

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ABSTRACT

The thesis has been divided into six chapters. The literature survey including several reported hydrogels based sensors and adsorbents are summarized as an introduction in Chapter 1. Scope and objectives of the research work discussed in chapter 2. In chapter 3 considering the toxicity of heavy metal ions we have developed a colorimetric sensor 11, 16-bis (phenyl)-6, 6, 21, 21-tetramethyl-m-benzi-6,21-porphodimethene (*meta*-BPDM) incorporated polyacrylamide/carboxymethyl guar gum (PAM/CMG) polymeric hydrogel. *Meta*-BPDM is an organic moiety containing pyrrolic and carbocyclic units insoluble in aqueous medium. Zn^{2+}, Cd^{2+} and Hg^{2+}, owing to their biological significant value and environmental harm, have attracted more attention. The selective detection of Zn^{2+}, Cd^{2+} and Hg^{2+} metal ions has always been challenging due to their closed-shell d^{10} electronic configuration which makes them spectroscopically silent. The *meta*-BPDM embedded hydrogel shows high stability, sensitivity and selectivity when it is dipped into the aqueous solutions of Zn^{2+}, Cd^{2+} and Hg^{2+} metal ions. During detection, the binding of these metal ions in hydrogel causes hydrogel to change from red to bluish-green which was visually detected and confirmed by UV–visible spectroscopy. The hydrogel was characterized by using solid-state UV–visible spectroscopy, scanning electron microscopy, X-ray diffraction, Thermogravimetric analysis, Fourier-transform infrared spectroscopy, Energy-dispersive X-ray analysis and its sensing properties were studied. The *meta*-BPDM-embedded polymeric hydrogel was found to be an excellent, selective colorimetric sensor for Zn^{2+}, Cd^{2+} and Hg^{2+} in aqueous medium without leaching of *meta*-BPDM from the hydrogel in presence of various other alkali, alkaline and heavy metal ions.

The selectivity to sense these ions is mainly dependent on the binding constant of these metal ions with the *meta*-BPDM embedded in the hydrogel. The sensitivity of the hydrogel was 0.5, 1, and 2 mg/L with Hg^{2+}, Zn^{2+} and Cd^{2+}, respectively. To the best of our knowledge, no colorimetric sensor is available to sense Zn^{2+}, Cd^{2+} and Hg^{2+} in aqueous medium based on colour changing molecule-embedded polymeric hydrogels. In chapter 4 subsequently applications of polymeric hydrogel explored for on-site visual naked-eye detection of spectroscopically silent Zn^{2+}, Cd^{2+} and Hg^{2+} metal ions in real industrial wastewater and of Zn^{2+} in E. coli bacterial cells. Chapter 5 discussed selective removal of Zn^{2+}, Cd^{2+} and Hg^{2+} ions from water. This hydrogel appears to be a competitive sorbent and has been successfully applied to efficient removal of Zn^{2+}, Cd^{2+} and Hg^{2+} ions from water in the presence of others. Batch adsorption experiments with respect to pH, initial metal ion concentration and contact time were also investigated. Chapter 6 discussed conclusion and future prospect of the work.

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List of Abbreviations and symbols

Abbreviation	**Full form**
AM	Acrylamide
PAM	Polyacrylamide
APS	Ammonium persulphate
MBA	N, N’-Methylene bisacrylamide
SEM	Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
TGA	Thermogravimetric Analysis
PHEMA	Poly (2-hydroxy methyl methacrylate)
BPDM	Benziporphodimethene
3-D	Three Dimension
IPN	Interpenetrating Polymeric Hydrogel
CMG	Carboxymethyl Guar gum
SPH	Superabsorbent Polymeric Hydrogels
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
GG	Guar gum
AAS	Atomic Absorption Spectroscopy
PPM	Parts Per Million
RPM	Rotation Per Minute
mL	Millilitre
M	Molar
Min	Minutes
gm	Gram
mg	Milligram

Chapter 1

Introduction

1.1 Hydrogels

Researchers, over the years, have given different definitions of hydrogels. Such as they are polymeric networks extensively swollen with water and retain significant amount of water within its structure, but insoluble in water. The hydrophilic functional groups attached to the polymeric network attributes to the absorbance and water retention property in a hydrogel. On the other hand, the cross-links between the polymeric chains attributes to their reluctance to dissolution. Hydrogels can be defined composed of two or more components having a 3-D network of polymeric chains. Hydrophilic gels are interpreted as networks of polymeric chains which are often colloidal gels having water as a medium of dispersion.[1,2] Hydrogels are commonly defined as a cross-linked polymeric chains that undergoes swelling in presence of water, and are obtained through a simple reaction between one or more monomers. It maintains its 3-D property in its swollen phase by the virtue of crosslinking.[3] Hydrogels have acquired huge attention in the past 50 years, due to their exceptional promise in various applications.[4] Hydrogels exhibit flexibility very similar to that of natural tissue due to their capability of carrying large water and fluid contents, such as biological fluids which may resemble biological tissues. Because of this property, great interest had been developed in designing the innovative devices by varying their physicochemical properties which can be tuned. Recently, natural hydrogels were gradually replaced by synthetic hydrogels having distinct structures that can be further modified to yield tailorable functionality and degradability. Relying upon the properties of the components utilized in polymeric network along with the density of the network joints, they can contain various amounts of water in equilibrium.[5]

The synthesis of hydrogels can be achieved by a number of chemical ways involving one-step methods like cross-linking of multifunctional monomers, polymerization, and multiple step methods which involves synthesis of polymeric chains containing highly reactive functional groups, which subsequently gets cross-linked with a suitable cross-linking agent. A polymer engineer can formulate polymeric networks possessing a molecular-scale control over structure including cross-linking density with modified features like, mechanical properties, biodegradation, biological and chemical response to stimuli.[6]

1.2 Natural Gums based Hydrogels

In the recent past, the prospected uses of natural gum polysaccharides in various aspects of water, food, energy, environment, biotechnology and medicine industries, have gained an eye of research fraternity, owing to their availability, low cost, structural diversity and remarkable properties. Natural gums or polysaccharides[7] are obtainable from various tree groups, possessing extraordinary properties, including renewable, biodegradable, biocompatible, non-toxic nature and can be easily modified chemically.[7] Hydrogels based on natural gums or polysaccharides provide several valuable properties compared to synthetic origin. In the recent years they have witnessed remarkable improvement as a novel alternative because of health, environmental pollution and ecological issues faced by the uncontrolled use of synthetic polymers based hydrogels.[8, 9] Hence, there is a great demand of the materials that do not harm the ecosystem. These hydrophilic polymeric networks are insoluble in water, display higher strength and elasticity.[1, 10] They are eminently responsive towards their environment, like any change in, pressure, electric field, solvent composition, pH and temperature.[11,12,13] The practical importance of these hydrated polymeric network is tremendously increasing day by day and are of interest as biomimetic, intelligent and smart materials. They have applications in sensors, actuators and frequently they are being studied as self-oscillating gels.[14] Hydrogels termed as Smart networks exhibit a significant physicochemical response towards small changes in the surroundings. These changes are reversible and have capability of returning to its initial state after the trigger is removed.[15]

1.3 Classification of Hydrogels

Based on source: They can be of natural or synthetic origins. Natural polymers including proteins such as collagen and gelatine and polysaccharides such as alginate, starch, cellulose, glucomannan, pectin, hemicellulose, gums, and agarose forming hydrogels. Synthetic polymers including polyvinyl alcohol (PVA), polyethylene glycol (PEG), polyacrylic acid (PAA), polyacrylamide (PAM) that form hydrogels are conventionally synthesized using chemical polymerization methods.[2]

Based on polymeric composition or synthesis techniques:

(I) Homopolymer hydrogels have basic structural and functional unit comprising of a single type of monomer in the polymeric network. They can have cross-linked skeletal depending on the polymerization technique as well as on the type of monomer.[16]

(II) Copolymeric hydrogels are derived from a variety of monomeric units with at least one hydrophilic component. The polymeric network chains can be arranged in a random, block or alternating configuration. [17]

(III) Multipolymer interpenetrating polymeric network (IPN) can be synthesized using two independent cross-linked natural or synthetic polymer component, confined in a network form. In case of Semi-interpenetrating hydrogel, one polymer is a cross-linked and other polymeric component is a non-cross-linked.[18] They interact without any chemical bonding between them, one straight polymeric chain penetrates into another crosslinked network.[19]

Based on physical structure and chemical composition: (I) Non-crystalline (Amorphous) (II) Semicrystalline, a composite of amorphous and crystalline phases. (III) Crystalline.[2]

Based on cross-linked networks: Chemically cross-linked networks have permanent bonding involving covalent interaction while physical networks have transient junctions involving entanglements of polymeric chain involving hydrogen bonds, polar or ionic, hydrophobic type of physical interactions.[2]

Based on electrical charge: (I) Neutral (non-ionic), (II) Ionic (including anionic or cationic), (III) Amphoteric having both acidic and basic groups, (IV) Zwitterionic (polybetaines) possess both cationic and anionic functionality in each repeating unit.[2]

1.4 Preparation of hydrogels

Hydrogels can be synthesized using natural, synthetic, and composite of both natural and synthetic polymeric materials. Cross-linking of polymer chain by chemical modification, external cross-linking agent, by exposure to high energy radiation and polymerization grafting have been utilized for the preparation of hydrogels. In the hydrogel formation chemical cross-linking involve the formation of new covalent bonds between polymeric chains in the hydrogel, where as physical cross-linking involves physical interactions between polymer chains.[53] Both physical and chemical methods have their own advantages and disadvantages related with them. Conventional and controlled radical polymerization techniques results hydrogels with various morphologies, size and composition including hollow core-shell particles.[54, 55] The most widely used mechanism is free radical polymerization to prepare hydrogels.[56, 57] Usually in hydrogel formulation, the gel reactants react with crosslinker (s) to form 3D-crosslinked networks in presence of radical initiators like potassium persulfate or ammonium persulfate. Free radical polymerization occurs in three main steps: initiation, propagation, and termination[58]. In the initiation step, free radicals ($R^{\bullet}$) are generated by the dissociation of an initiator and then react with other molecules (M) to produce the first radicals $M^{\bullet}$. In the propagation step highly, reactive free radicals rapidly react with molecules of monomer resulting formation of macroradicals. Usually, termination occures by combination or disproportionation reaction of free radicals. Various shape of hydrogels like bulk, sphere, and films can be obtained by selecting the appropriate preparation process, raw material, and polymerization condition.[47]

Bulk Hydrogels: Usually, they are smoothly obtained by solution or homogeneous polymerization wherein all the reactants i.e., the monomer (or polymer), initiator, and cross-linker are soluble in the medium. The resultant hydrogel generally takes up the shape of the container in which it has been polymerized and yields a relatively homogeneous hydrogel.[59] However, due to the slow diffusion of solute to the adsorption sites within hydrogel it will take long time to reach equilibrium during water treatment.[60] Usually, bulk hydrogel is cut into small sized pieces manually or by using food blender to produce small size hydrogel beads for better adsorption efficiency. However, sometime cutting or grinding step may yield hydrogel particles with polydispersity and damaged morphology.[61, 62]

Spherical Hydrogels: Spherical hydrogel does not require grinding or cutting and thus avoids further morphology destruction and energy consumption. Hydrogel bead is one of the examples of spherical hydrogel with a millimetre diameter. Generally, synthesis of spherical hydrogels involves dropping the monomer or polymer suspension using syringe into a solution thus, the size of the resultant hydrogel bead is usually dependent on the diameter of the syringe. Chitosan, a natural polysaccharide which is biodegradable, nontoxic, odourless, biocompatible and biopolymer is commonly used for hydrogel bead preparation. It can be crosslinked by contacting with sodium and potassium cations.[63-67]

Hydrogel Films: Hydrogel composite film seems to have a great potential for real application. They exhibit robust and repeatable self-healing behaviour in the aqueous medium and are easy to prepare. Many hydrogels have been used as an efficient ion-exchange film for water purification. Recently, the electrospinning technique is selected as a method to directly synthesis nanofiber hydrogel film.[68] In order to synthesize a particular hydrogel composite with desired properties, some additional components could be incorporated into the hydrogel film either by mixing additive with hydrogel precursor before polymerization or by grafting after polymerization.[69] Usually, hydrogel film is used in sensing applications in which it is generally employed as an active membrane, primarily to provide more hydrophilic surface and less susceptible to contamination.[66]

1.5 Characterization of Hydrogels

Various types of characterization techniques have been utilized for understanding the hydrogel's physical and chemical properties. The physical properties of polymeric hydrogels determined by the volume fraction, effective molecular weight of the polymeric chain in between two crosslinking junction and on the density of the crosslinking.[20] Hydrogels have many properties, such as absorption capacity, permeability, swelling behaviour, optical, surface, and mechanical properties. The nature of the polymer chains and the crosslinking present in the network structures play a significant role in the outcome of the properties of the hydrogel. All these properties are responsible for making hydrogel a promising material for a wide range of applications.[21]

Fourier Transform Infrared Spectroscopy FTIR analysis: This technique provides an authentic data about the crosslinking and give an idea about morphology of hydrogels.

Atomic Force Microscopy (AFM): This technique helps to examine the surface morphology of the hydrogels. It uses multimode atomic force microscope.

Network Pore Size: Various techniques, for instance, Quasi-elastic laser light scattering, mercury porosimetry, rubber elasticity measurements, electron microscopy, and equilibrium swelling experiments are employed to find out the network pore size of hydrogel. This is an important technique for hydrogel characterization.

X-ray Diffraction: X-ray diffraction analysis enables one to understand the crystalline and amorphous nature of hydrogel, whether the crystallinity is maintained or was deformed while synthesizing.

Swelling Behaviour: In order to study the potential use as a hydrogel, the specific swelling data studies are employed and many researchers have successfully worked upon it.

Crosslinking and Mechanical Strength: The crosslinking density inside the network structure of hydrogel determines its mechanical strength. Generally, with increasing crosslinker concentration mechanical strength of the hydrogel also increases.

Rheology: It depends on the type of interactions (association, entanglement and crosslinks) present in the polymeric network among polymer chains.

All these characterization methods provide important information about the desired crosslinking results, formation of hydrogel. Which can be useful further for various applications.[3]

1.6 Applications of Hydrogel

The salient features of hydrogels, they are biodegradable, hydrophilic character, biocompatible, less toxic, highly flexible similar to tissues and easily modifiable. They have good transport properties and the ability to response towards environmental changes such as pH, temperature, or the concentration of metabolites. Owing to their extraordinary properties, hydrogels are said to have novel applications in a number of fields like wound dressing, drug delivery, agriculture, tissue engineering, water purification, hygiene applications, etc.[3,7]

Owing to the properties similar to human soft tissue, hydrogels have been frequently utilized in biomedical field, such as drug delivery.[22-25], gene vectors, tissue engineering[26, 27], and biosensors[28, 29]. Hydrogels meet both material and biological requirements because they have unique characteristics like desired functionality, reversibility, and biocompatibility. They are commonly used for cell-laden, tissue regeneration, drug delivery, and biosensor.

Soft Contact Lenses: It remain one of the most widely used applications of hydrogels due to their biocompatibility and mechanical properties. Hydrogels have the adjustability towards the global ocular curvature and allow the atmospheric oxygen to reach up to cornea by dissolving the water of the lens.[30] Polyhydroxyethylmethacrylate (PHEMA) was the first ever established synthetic hydrogel as a favourable and great candidate for manufacture of contact lens by Wichterle and Lim (1960).[3]

Tissue Regeneration and Tissue Engineering: The loss or chronic failure of any organ function due to some severe disease or accident necessitates the demand of tissue and organ transplantations. It has become challenging due to lesser availability of donors, social norms, legal norms etc.[31] Tissue Engineering has developed a hope for designing an ideal living substitute which imitate the functions of living tissues in human system.[3] Scaffolds act as 3-D artificial templates in which the rebuilding of targeted tissue is cultured to grow. The extremely porosity of hydrogel enables the diffusion of cells during migration, transfer of nutrients and excludes the unwanted products outside of cellular membranes.[32] Now, both synthetic and natural hydrogels are used as scaffolds in many tissue engineering applications, including repair of tendon, cartilage, ligament, blood vessels, skin and even heart valves.[33] They have been utilized in various biomedical applications such as fillers for aesthetic correction of scars[7], bladder[34], cartilage[35], orthopaedic applications[36], skin[37] and bone[38]. Polysaccharides based hydrogels that exhibit biocompatibility with tissues which makes them more significant for biomedical and tissue engineering applications.

Wound healing: Injured skin is covered to avoid bleeding and to protect the wound from environmental infections. Wound dressings are non-toxic, antiseptic, permeable to oxygen, preserve wound moisture, cause minimum damage, eliminates excess exudates and thus fasten the healing process while direct interacting with the wound. A great advantage of gum based hydrogel in wound dressings is that they can easily be applied or removed without interfering with the wound beds.[39, 40] The mechanical properties of hydrogels increase its elasticity and flexibility to adapt with wounds and bring instant relief to patients in pain, as compared to conventional bandages, pads or gauzes. They act as a coolant to localized wound in case of burn also reduces the pain and recovers from resultant damage.[41, 42] Non-adhesive nature and hydrophilic surface of hydrogels do not allow it to attach with cells therefore causes less pain and discomfort to patient. Hydrogel transparency has an advantage over traditional bandages as it causes less pain during peeling it off. Various hydrogels for wound dressings are available, like amorphous gels, gel-impregnated gauzes, plasters or sheets. The development of hydrogel formulations to address different aspects of wound healing and management such as easy dressing, reduction in infection is attaining new heights.[43, 3]

Drug Delivery: The porous structure of hydrogels can provide a matrix for drug loading or delivery while protecting drugs from hostile environment at the same time. Hydrogel targets specific sites like colon as a drug delivery agent and release drug or other nutrients timely. In addition to this hydrogel interacts very less with the drug and other loaded solute hence sustained and prolonged release occurs in the larger fraction comparative to conventional drug delivery systems.[7] The unique property i.e., hydrophilicity of hydrogels enables to hold excessive amounts of water which make it useful in drug delivery application that control release of solute over a given time period. Numerous biomaterials have been explored for this purpose, which act by two mechanisms (1) controlled release of drug may be achieved by varying the crosslinker amount and monitoring the ratio of hydrophilic to hydrophobic monomers. (2) Hydrogel release large fraction of active drug molecules (protein and peptides) because its interaction with drug is very less. Targeted and controlled drug delivery would decrease the undesired side effects and support the recovery aspects. Several mechanisms express the release of drug from hydrogel such as (a) diffusion, (b) chemical control, (c) deswelling and environmentally responsive release.[3]

Agricultural Applications : Water management is a notable footstep for accomplishing sustainable development and growth in agriculture[44]. Superabsorbent polymeric hydrogels SPH based on natural polysaccharides exhibit ability to hold and retain huge amount of water thus gaining importance in agriculture. Prolonged moisture can be retained by addition of SPH to the soil in arid and semi-arid areas so that crop can withstand harsh climatic conditions. Hydrogels function as ‘mini liquid tanks’ in arid and semi-arid soil, releasing water along with desired loaded nutrients into the soil. Modification in hydrogel properties as required give fertile physical properties of soil.[45] The usage natural polysaccharides based SPH is flourishing owing to their biodegradability, durability, high water holding ability, avoid loss of nutrients, nontoxic, and their sustainability compared to synthetic polymer based hydrogels.[46] Hydrogels have been used for the prevention of soil erosion over a decade by reduction in soil erosion, increasing water holding capacity, enhancing permeability of finely textured soils, improve water infiltration among fine-textured agricultural soils. The water-soluble polyacrylamide (PAM) hydrogels form a thin film covering soil surface and are very efficient in preventing soil erosion. This film protect soil surface from washing away during irrigation and retains the optimum water content within the soil system, so that irrigation water can permeate easily.[3]

Hydrogel as adsorbent: As we all know emerging contaminants including pharmaceuticals, pesticides, industrial chemicals, metal ions, surfactants, and personal care products have raised global concern for their significant hazard to aquatic ecosystem and human health. Many of them have no regulatory standards on the effects of chronic exposure due to the lack of information.[70] These contaminants are stable under various conditions such as aerobic digestion, heat and light thus they can accumulate and cause adverse effects on ecosystems. Therefore, adsorption method has been greatly adopted to treat emerging contaminates as it is cost-effective and highly efficient.[71]

There has been a growing interest in exploring hydrogel as adsorbent in the application of pollution control. The adsorption process strongly depends on the nature of adsorbate as well as on the hydrogel adsorbents. The adsorption data of emerging contaminates on hydrogels can be well interpreted by the Freundlich model and Langmuir model, with the kinetic model usually pseudo-second-order. Hydrogel adsorbents have strong affinity for pollutants predominantly due to the various interactions between adsorbate and adsorbent, including hydrophobic interaction, hydrogen bonding, ionic or electrostatic interaction, and π–π interaction. This varies according to the chemical nature of adsorbent and adsorbate, pH, adsorbent dose, the ionic strength of the solution, and so on. When the solution pH is different from the isoelectric point of hydrogel adsorbents, the surface of adsorbent will carry ionic charge. At the same time, ionic adsorbate also gets protonated or deprotonated at different pH values, this results electrostatic interactions between them. Hence, pH is an important factor responsible for adsorption mechanism.[47, 3] Many solid and liquid phase removal trials remained tracked for the elimination of pollutants from liquid such as coagulation, adsorption, biochemical precipitation, photodegradation, ion exchange, electrochemical treatment, flocculation, and membrane percolation.[48-51] Among these various techniques, adsorption owing to its high efficiency, minimal effort and simplicity considered better than other techniques. Hydrogels are considered unique for water refinement by adsorption due to their porous structure, high absorption capacity, low crystallinity and abundant in functional groups. Polysaccharides (Gum) contain various important functional group in their structure, in this way, hydrogel based on them and graft copolymers have been largely explored as adsorbents for the elimination of pollutants such as heavy metal ions and organic dyes from aqueous media. The principle advantage of using natural gum-based hydrogels as adsorbents is their biocompatibility, their structure can be easily tailored according to the nature of the pollutant.[52] Although hydrogels are found to be superior candidate for the removal of a wide range of aqueous pollutants, including heavy metals, dyes and other emerging contaminates but selective adsorption of contaminates is rarely explored. Therefore, research efforts are required to develop hydrogels with the desired properties, sensitivity and selectivity toward a specific pollutant. Many hydrogels have been developed with desirable strength and adsorption capacity, but their chemical and biological stability always ignored which needs to be considered in wastewater treatment for economic viability and sustainability.[47]

Hydrogel as sensor of heavy metal ions in environmental and biological sample (targeted application): Nonbiodegradable heavy metal ions widespread existence in water are potentially threatening to the ecosystem and living organisms. Hydrogels have been functionalized with many biomolecules, including DNA, to form stimuli-responsive sensors and materials[72,73] However, for sensing application most of them rely on hydrogel phase transition or volume change. Hydrogels are ideal for optical sensor immobilization due to their good biocompatibility, large sensor loading capacity, and very low optical background. Moreover , hydrogel backbone property such as charge and hydrophobicity can be modified by mixing with different monomers, allowing further control of sensor performance.[73] The stimuli-responsive hydrogel can be used as a transducer material for transforming the reaction of a recognition unit into a physical signal, which can be detected by, e.g., quantifying the change of optical length with an optical fibre, observing the resulting change in swelling pressure under isochoric conditions or by measuring the diffracted wavelength of a polymerized crystalline colloidal array. The host-guest interactions in sensing applications have been proven to be a powerful tool. Usually, macrocyclic polyethers, i.e., crown ethers have been proved to be promising candidates in combination with hydrogel facilitated by the generation of highly selective and reversible host-guest complexes with specific alkali and heavy metal cations. Notably, colorimetric sensing method has attracted considerable attention because of its ease of operation, low cost, rapidity, and direct visual perception. To have better sensitivity, most colorimetric sensors are diffused in sample solution for full interaction with the target substance, but sometimes an uneven and unstable dispersion of the sensors induces unsteady detection results. To avoid this problem, chemo sensor can be assembled on a solid substrate. The selection of a solid substrate is most important as it can considerably affect the sensitivity of the sensor. In the sensor studies, a colorimetric chemo sensor can be formed by the design of molecules that change their colour in sample solution due to an alteration in their molecular structure in the presence of target ions.[74] The solubility of the designed sensor molecule is important in aqueous media. One of the most important issues in these studies is the fact that pollutant species i.e., anion or cation are soluble in water, but the sensor cannot dissolve directly in water. Moreover, the soluble sensor is only suitable for a single use. Researchers have chosen to polymerize the molecules with sensor characteristics to stand with such problems. In this view, the sensor must be insoluble to be used again and can be easily removed from the sample solution. The best example of a solid support or polymer, which can be easily removed from the sample solution with a filtering process, is hydrogel. They are important for various sensing applications as they can be synthesized with good yield, have swelling in water, are reusable and stimuli responsive.[74,75]

Among other sophisticated technique such as atomic absorption (AAS) spectroscopy, inductively coupled plasma (ICP) spectroscopy which needed additives that are time consuming and complicated. Hence formulation of a new sensing methods for simple, fast, and portable on-site detection of multiple metal ions is considerable research interest. A colorimetric hydrogel sensor can act as an indicator which can produce visual changes in the presence of metal ions. The colorimetric probe has many binding sites like -OH, -NH and -SH functional groups that can form water-insoluble and stable complexes with various metal ions under ambient conditions. The colour change mechanism involved chemisorption process. Which implies the electron transfer mechanism occurring between adsorbent (sensor) and adsorbate (metal ions).[76]

Stimulus-sensitive hydrogels give response to slight changes in their environment such as physical stimuli including temperature, pressure, electric field, light, ionic strength, and magnetic field, chemical stimuli for example pH or ions change, or biological stimuli by changing volume in antigen, glucose, and enzyme. The hydrogels in the presence of these stimuli experience phase transition by sensing target substrate and simultaneously transform this sense into a macroscopic event. Such hydrogels may act as active sensing material and their response time depends on the shape, size and composition of hydrogel and can be improved by increasing both the number of ionic groups, and pore size and by reducing the size and cross-linking density.[77] Polysaccharide-based natural polymers, including cellulose, starch, protein, chitosan and their derivatives, have also been explored in hydrogels synthesis for sensing applications, because, moreover to their ample functional groups and special chemical or physical properties, they are more interesting than their synthetic analogues which make them suitable for sensing. Hydrogels embedded with ion sensitive component can provide a great way of sensing ions, their concentration, and pH. Hydrogels based on polyacrylamide because of excellent biocompatibility and well-defined synthesis protocols with desirable physiological and mechanical functions are widely used in biosensors.[78]

Hou formulated an injectable hydrogel based on polysaccharide/polyacrylamide system for high-performance strain sensors.[79] Hydrogels based on PAM and photonic crystals have also been explored as glucose or pH sensors by tracking the ionic strength. In addition to photonic crystal sensors, PAM hydrogels were immobilized with protein, enzymes, peptides, or antibodies for molecular recognition. They have been used humidity sensing, in the form of composites, because of their super absorbency.[78]

Amine-functionalized polyacrylamide hydrogels cross-linked with 5,6-dicarboxylic fluorescein are more selective for Cu^{2+} in presence of other metal ions and can be used to detect and quantify cupric ions.[80] Toxic heavy-metal ions (Hg^{2+}) may be identified by polyethylene glycol diacrylate (PEGDA) hydrogels by judicious exploitation of optical waveguides. The material allows to modify smooth surface with minimal light scattering at the surfaces. The fluorescence of embedded carbon dots (CDs) can be used to detect absorbed metal ions.[81] Other mechanisms including fluorescence red shifts upon Hg^{2+} ions binding can be used through exploitation of thymine rich DNA-polyacrylamide hydrogels.[82]

The colloidal photonic crystal hydrogel (CPCH) films functionalized with aptamer were employed for the visual recognition of heavy metal ions (Hg^{2+} and Pb^{2+}). The CPCHs were obtained from a colloidal crystal arrangement of monodisperse silica nanoparticles, polymerized inside the polyacrylamide hydrogel and aptamers were then cross-linked within hydrogel network. The specific binding of target ions and single-stranded aptamers cross-linked in the hydrogel network caused the hydrogel to shrink during detection. Which was identified as a corresponding blue shift in the Bragg diffraction peak position of the CPCHs and used to estimate the amount of the target ion.[83]

Diehl et. al. discussed the rapid mechanical actuation and sensing performance of plasmonic nanostructures combined with responsive polymeric network.[84] Stimuli-responsive DNA-based nucleic acid hydrogel system and their novel applications have been reported.[85] Recent developments about enzyme-responsive polymeric assemblies, nanoparticles, hydrogels and discussed their promising applications in biocatalysis, drug controlled release, sensing, imaging, and diagnostics.[86] The molecular recognition properties of analyte-responsive hydrogels, the physicochemical changes occurs upon analyte binding can be used to generate a detectable signal for sensing applications and how these materials have been incorporated into sensors and drug delivery systems have been reported.[87]

1.7 Literature Survey

1.7.1 Guar gum (GG), Carboxymethyl guar gum (CMG) and Polyacrylamide (PAM).

Guar gum (GG), belong to the galactomannan family, is a natural polysaccharide extracted from the seeds of Cyamopsis Tetragonolobus leguminous plant which is grown in India and is currently used as an edible item. Guar gum is one of the most important water-soluble, naturally occurring and non-ionic polysaccharides. It also finds application in various industries as viscosity builder and water binder. The common structure of GG as shown in fig.1. having a linear chain of β-1,4-linked D-mannose units (M) as the main backbone, linked by α-1,6-linked D-galactopyranose residues (G) as the side branches. The most general arrangements of the galactose branches to occur in every other mannose unit. The precise ratio of mannose to galactose unit (M/G) is depend on its origin and climatic conditions. The molecular weight of GG is the highest among all known natural polymers produced of industrial gums causing it to form highly viscous solutions at low polymer concentrations.[88] GG is extensively used in various industries such as oilfield[89], pharmaceutical industry[90], food[91], paper, textile[92] and cosmetic[93]. Different techniques are used for processing of GG which depends on the end products. Guar gum has been tailored by various methods such as derivatization, grafting and network formation to enhance its properties for a wide range of applications. Generally, guar seeds are dehusked to allow guar splits, then frequently it is crushed to obtain powder form of guar gum which is easily soluble in water. High molecular weight guar gum undergoes great intermolecular hydrogen bonding resulting in a highly viscous solution, but some limitations are associated with it such as unrestricted and incomplete hydration at room temperature, low thermal stability, bad clarity of the solution and high susceptible to microbial degradation which limits its application in industry. Therefore, some chemical modifications are required to overcome these limitations with enhanced properties like swelling, solubility and stability. Modified GG has a significant use in petroleum production, mainly, in hydraulic fracturing operations.[93] The grafting on Guar gum with acrylamide[94], methacrylic acid[95], acrylic acid[96], N-isopropylacrylamide[97], ethyl acrylate[98], acrylonitrile[99], methyl acrylate[100] and methyl methacrylate[101] has been reported. Chemical modification of guar gum to produce guar gum derivatives includes reaction of the hydroxyl groups.

Carboxymethylguargum (CMG) is very important guar gum derivative, because it covers a broad range of industrial applications. The polysaccharide backbone is similar to guar gum, a galactomannan. The polar carboxyl group offers CMG a strong hydrophilic water soluble commercial polysaccharide and so it can be used in the production of superabsorbent hydrogels. Carboxymethyl guar gum (CMG) is an anionic guar gum derivative with good transparency, good stability, high viscosity dissolution speed, and with low price. Many laboratory procedures have been developed to synthesize carboxymethyl derivative of guar gum. CMG is obtained by reacting monochloroacetic acid or its sodium salt with deprotonated guar gum. Strong base, like sodium hydroxide, is required to activate hydroxyl group of GG for the nucleophilic substitution.[94]

Polyacrylamide is a water-soluble polymer consists of a hydrophobic main chain and hydrophilic functional groups present in side chains. Swelling of PAM is not greatly affected by the presence of electrolytes or varying pH of the medium. The function of amide group is to introduce the possible ionic functionalities in the gel.[102] In addition to this polyacrylamide readily forms hydrogen bonding with water and when copolymerized with biopolymer expected to be more water absorbent. Synthesis of hydrogels based on polyacrylamide and carboxymethyl guargum (PAM-Cl-CMG) by using initiator potassium persulphate and cross linking agent N, N'methylenebisacrylamide have been reported. Swelling percentage was selected as a parameter for determining the best combination of hydrogel in each series of CMG concentration. The obtained results show that the swelling percentage is directly proportional to the concentration of carboxymethyl guar gum and inversely proportional to the concentration of crosslinker[16].

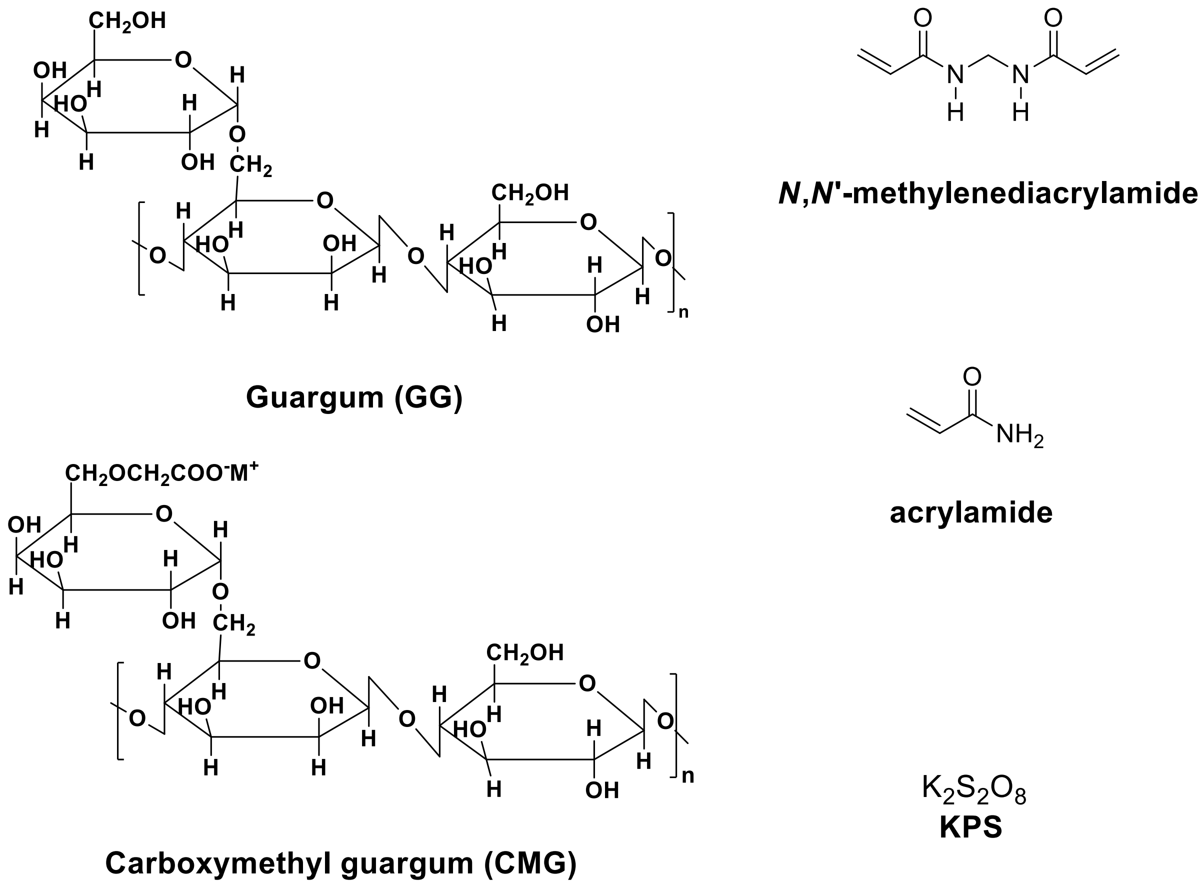

Figure 1.1. Structure of Guar gum (GG), Carboxymethyl guargum (CMG), Acrylamide (AM), N, N'methylenebisacrylamide (MBA) and Potassium Persulphate (KPS).[103]

1.7.2 *meta*-benziporphodimethenes

meta-Benziporphodimethene was firstly synthesized by Martin Stępień during his research works of Ph.D. thesis. This is a partially reduced form of *meta*-benziporphyrin. Those synthesized benziporphodimethenes obtained from *m*-benziporphyrins oxidation were alkoxy and hydroxy analogues. Actually, *meta*-Benziporphodimethenes are modified *m*-benziporphyrins having two tetrahedral meso carbon atoms at 6 and 21 positions. (Fig. 1.2) It is to be noted that *meta*-benziporphodimethenes are non-aromatic due to structural limitation as the ring current attenuated due to tetrahedral meso carbon atoms.[104,105]

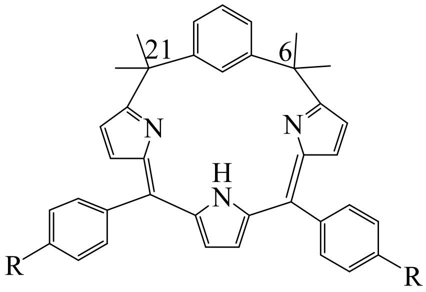

Figure: 1.2 Chemical structure of *meta*-Benziporphodimethene.[105,106]

m-Benziporphodimethenes can be synthesized in good yield by the synthetic procedure adopted by Latos Grażyński and Martin Stępień, involving Lewis acid catalyzed condensation of pyrrole, $\boldsymbol{\alpha}$, $\boldsymbol{\alpha}$'–dihydroxy–1, 3–diisopropylbenzene and an aromatic aldehyde in a fixed ratio. This reaction yield was found to approximately 27%.[104,106] (Fig. 1.3)

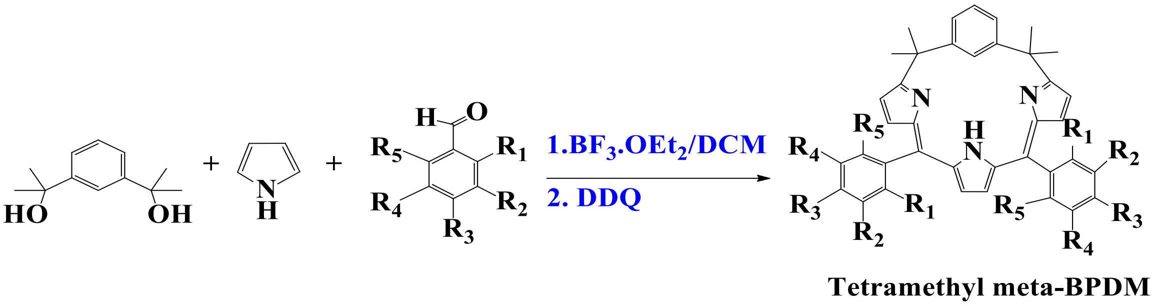

Figure: 1.3 Synthesis of *meta*-benziporphodimethenes.

meta-Benziporphodimethenes are normally red color compounds. They show a broad UV-Vis spectrum due to discrete conjugated system. In *meta*-benziporphodimethenes high energy Soret band is observed at about 350 nm and lower energy Q band is observed at about 510 and 550 nm approximately.

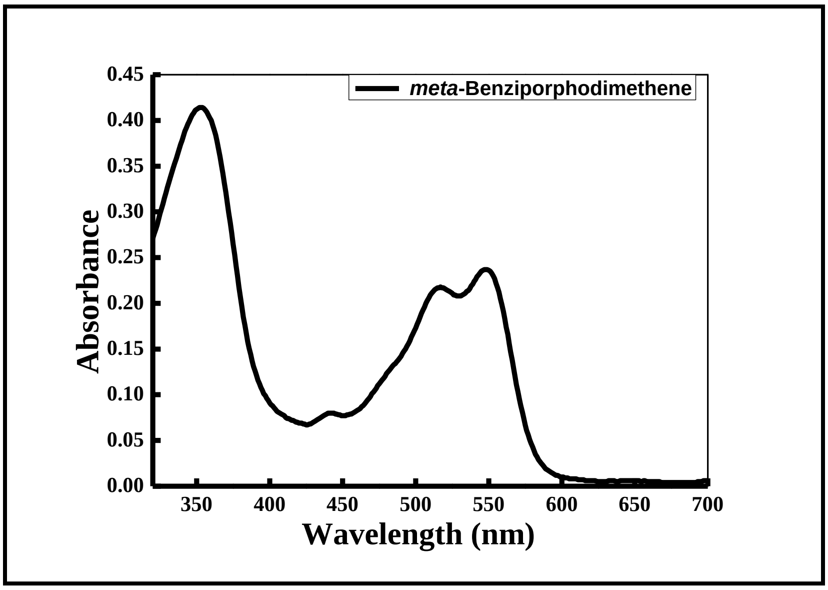

Figure: 1.4 UV-Vis Spectra of *meta*-Benziporphodimethene[107].

1.7.3 Metal complexes of *meta*-Benziporphodimethenes

The Zn, Cd, Hg, Ni and Ag[108] complexes of *meta*-benziporphodimethes have been reported so far which are quite stable also. Latos Grażyński and co-workers in 2004 have reported metal complexes of *meta*-benziporphodimethenes with zinc, cadmium, mercury and nickel.[104] Later Hung and co-workers also reported the metal complexes of *meta*-benziporphodimethenes with Zn, Cd, Hg and Ag showing for hydrogen bonding, agostic metal arene interaction, η^2 and π coordination.[108] The general synthetic procedure involves mixing of free-base m-benziporphodimethenes with anhydrous metal salt in presence of mild base 2, 6-lutidiine in mixed solvents of acetonitrile with either chloroform or dichloromethane. The metal complex formation is indicated by change in color of solution from red to greenish blue in minutes after mixing at room temperature. Evaporation of solvent invacuo under reduced pressure yields the metal complex and the crystals can be obtained by crystallization using hexane solvent.[109]

1.7.4 Fluorescence enhancement property of *meta*-benziporphodimethenes and its explored applications

These compounds possess an important property that they are non-fluorescent in free-base form but fluorescence turn on upon zinc metalation with no background emission.[105] The crucial part of this finding is that *meta*-benziporphodimethenes act as a selective sensor for zinc ions in presence of cadmium and mercury ions[110]. Comparatively very less fluorescence is observed for cadmium and mercury ions. This kind of fluorescence which switch on upon metalation comes under the category of ''**chelation enhanced fluorescence''(CHEF)**. Mostly CHEF sensors are based on fluorophores, such as fluorescein, anthracene and dansyl which emit at wavelength shorter than 600 nm. Sensors that emit above 600 nm, having minimum background emission, cause lesser light induced tissue damage, penetrate effectively and have less scattering in optically diffuse samples.[109] It is important to note that these kinds of molecules do not form complexes with alkali, alkaline earth and other some transition metals which are physiologically important as shown by Hung and co-workers.[105] Hung and coworkers also found that the stability constant of *meta*-benziporphodimethene zinc complexation is greater than the cadmium and mercury respectively.The main reason for this observation is planarity of the macrocycle in the bind state. The free-base macrocycle exists as highly distorted non-planar molecule, but on metalation the tripyrrin moiety becomes planar. In the complex metal ions occupy a tetrahedral coordination site composed of three nitrogens of tripyrrin moiety and a chlorine which sits at the axial position.[105]

Zinc ions can be found throughout the human body in bound state with protein as structural cofactors , gene expression regulator**,** labile pool of zinc ions in the vesicles of neurons and Zn^{2+} is also an important regulator of the cellular apoptosis.[111] They are involved in various biological processes in the human body. While a disorder of zinc metabolism can cause severe diseases such as Alzheimer's disease[112] , Parkinson's disease[113] and patients with inflammatory diseases, tumors also show abnormal Zn^{2+} concentration.[114] The vital roles and toxic influences of Zn^{2+} are commonly observed therefore, real-time detection of Zn^{2+} may help to discover its physiological and pathological roles. Keeping such crucial application in mind Hung and co-workers have developed an organic hydrogel film for real-time and free from indicator detection of zinc ions in the solution with micron-sized pillar array by embedding a fluorescent indicator 11,16-bis(phenyl)-6,6,21,21-tetramethyl-*m*-benzi-6,21-porphodimethene in a hydrogel host poly(2-hydroxyethyl methacrylate). The organic hydrogel film shows high stability and selectivity to Zn^{2+} ions. The sensitivity of the sensing film was enhanced by increasing the surface area via fabricating a micron-sized pillar array on the surface of the hydrogel sensing film. The response time for Zn^{2+} concentrations of 10^{-4} and 10^{-3} M, was found to be around 30 and 3 s, respectively.[110]

Recently, Kumar and his coworkers have explored these *meta*-benziporphodimethenes for cellular imaging of zinc ions in MDA-MB-468 breast carcinoma cells and observed that they are lesser cytotoxic for longer time and can internalize successfully. Further, they can be used for selective sensing of intracellular zinc ions. The electron releasing and withdrawing substituent at meso positions does not impact on internalization. Though, *meta*-benziporphodimethenes also respond to Cd^{2+} and Hg^{2+} ions but their concentration in healthy cells rarely present so will not interfere in imaging of Zn^{2+} ions in healthy cells.[115]

1.7.5 Heavy Metals and Toxicity

The heavy metals are toxic bio-accumulative, non-biodegradable pollutants of the environment that pose a risk to human health. Heavy metals, such as arsenic, mercury, cadmium, lead, etc., are well-known bio accumulative, highly toxic, non-biodegradable pollutants of the environment. Increased urbanization, industrialization and natural calamities such as volcanic activity, erosion of minerals and leaching of deposited ores are responsible for an increased level of heavy metals in our environment.[116] Living organisms require small quantities of heavy metals such as manganese, iron, cobalt, copper and zinc. These are nutritionally essential for the regulation of human metabolism. Although all metals are toxic at higher concentration, heavy metals, such as cadmium, mercury and lead, are toxic even at lower levels.[117] Heavy metals such as lead, mercury and plutonium have no known vital role in organisms but can cause serious illness due to their accumulation over time in the bodies of animals.[118] These metal ions aggregate in the human and animal bodies through the food chain, ecological system induces irreversible pollution and causes some serious health issues such as cancer, organ damage, nervous system damage and sometimes death.[119] Though, metal ions play vital roles in biology, but even nectar is a poison if taken to excess. Thus, surplus levels of metal ions in living bodies can lead to malfunctioning in respiration, growth, gene transcriptions, enzymatic reactions and immune functions.[120] Therefore, routine detection of heavy metal ions is important for the environment. Current techniques, such as AAS, ICPMS, X-ray fluorescence, etc., require expensive equipment, complicated and time-consuming methods and high levels of operator skills. The cost-effective, simple, fast, facile toxic metal ion detection method that allows real time on spot detection of heavy metal ions is an important goal.[121]

Among the most common pollutants found in wastewater, heavy metals are the main pollutants and causes severe ecological problems, thus their elimination from water during water treatment is crucial and requires research attention.[122] The wastewater contaminated with toxic heavy metals released directly into aquatic ecosystems including with or without pre-treatment.[123] These metal ions may accumulate to very high toxic levels without any visible sign. Long term irrigation with such heavy metal ion contaminated wastewater creates a problem for safe rational use of agricultural soils. Excessive agglomeration of heavy metals like Cd, Cu, Cr, Zn, Hg, Pb, Mn etc. in agricultural soil affects food quality adversely. Plants and vegetables cultivated in the nearby zones of industrial areas show increased levels of heavy metals. This accumulation of heavy metal ions in edible and nonedible items is enough to cause clinical problems to both human beings and animals consuming that. Therefore, early detection, determination and elimination of heavy metal ions from effluents are important for the survival of living organisms.[124,125]

The monitoring of Zn^{2+} in living cells and tissue is very crucial owing to its predominant functions as signalling agents to mediate processes such as gene expression, neurotransmission, apoptosis, cell growth and division.[126] Disturbance of zinc homeostasis in human bodies have resulted in health disorders like Alzheimer's disease, diabetes, and several neurodegenerative disorders.[115] Furthermore, living organisms have the tendency to take up and accumulate death-dealing metals from the environment that are not necessary for their survival and can instigate intoxication in the body. For instance, cadmium is one of the most common toxic metallic pollutants even at very low concentrations. Cadmium has detrimental effects on humans causing brain development disorders, chronic inflammation to the heart and kidney, renal dysfunction, and impairing reproductive systems. Cd^{2+} ions are used in phosphate fertilizers, and may be generated by waste incineration and fossil fuel burning. Subsequently, it easily passes into the environment through industrial wastewater.[127] Another hazardous metal ion that is often absorbed by living organisms is mercury. Hg^{2+} ions have high affinity for thiol groups (-SH) present in proteins and enzymes. Consequently, the presence of Hg^{2+} ions in human bodies leads to the dysfunction of cells in the kidney, brain, and central nervous system. It is highly desirable to monitor Zn^{2+}, Cd^{2+} and Hg^{2+} ions, efficiently and sensitively. Therefore, the need of the hour is to develop a novel probe for the detection of these metal ions in both biological and environmental systems.[128,129]

1.7.6 Heavy metal ions sensors

Recognition of metal ions using fluorescent molecules has been carried out a lot in the literature.[130-134, 113] Notably, a highly selective and sensitive fluorescent chemosensor for Zn^{2+} and Al^{3+} based on europium complex with ligand 1,10-Phenanthrolin was reported by Pu, Fan and their co-workers and shows remarkable colour changes.[135] Furthermore, a fluorescent sensor based on diarylethene with a pyrene unit for the onsite detection of Cd^{2+} and Zn^{2+} in real water.[136] A highly sensitive fluorescent sensor based on diarylethene was used to detect Zn^{2+} and showed 27-fold increase in fluorescence intensity.[137] Later, Ding and co-workers used Salamo-type bisoximes and demonstrated them a relay-sensor for Zn^{2+}/Cu^{2+} and further use of their complexes for successive sensing of H^+ /OH^-.[138] Also, diarylethene salicylhydrazide Schiff base derivative was explored for Al^{3+} and Zn^{2+} sensing and their bio-imaging in live cells was also reported in the literature.[139] Supramolecular gel-based multi-analyte sensor array was also reported by Zhang and co-workers.[140] Pu and co-workers also reported the turn-on fluorescent chemosensor for the detection of Zn^{2+} based on the diarylethene derivatives.[141]

Fluorescent probes have emerged as powerful tools, owing to their high sensitivity, simplicity, quick-response ability and reproducibility. A variety of zinc ion sensors have been developed based on various fluorophores including BODIPY, anthracene, coumarin, fluorescein and quinolone.[142] Although the detection ability of these sensing probes is impressive, but they still suffer from some drawbacks such as low selectivity, complicated synthesis and poor selectivity. Therefore, there is a need of developing fluorescent sensors for the selective and sensitive detection is an ongoing research endeavor. The synthesis of fluorescent sensor based on 1,8-naphthalimide as fluorophore modified with 2,2 -dipicolylamine (DPA) receptors through an amide linkage for the detection of Zn^{2+} in aqueous solution have been reported. The fluorescence intensity enhanced on addition of Zn^{2+} to the solutions of sensor, ranging between 2.5 and 14 folds.[143] The DPA component is specific for Zn^{2+} so has been frequently used for Zn^{2+} over alkali and alkaline-earth metal ions exist in higher concentrations in biological samples.[144] On the other hand, 1,8- naphthalimide derivatives have good photostability and strong yellow-green fluorescence are extensively used as environmentally sensitive fluorophore for sensing of metals and other ions.[145] An amide linkage was introduced in between the DPA and naphthalimide fluorophore in order to increase the inflexibility or rigidity of the receptor or ligand scaffold. Which may provide a right coordination geometry for the receptor for enhanced Zn^{2+} selectivity.

Unlike linear conjugated oligopyrroles, the porphyrins macrocyclic framework is rather rigid, and metal complex formation cannot significantly improve the rigidity. Consequently, upon coordination to metal ions, say Zn^{2+} fluorescence cannot be drastically enhanced Therefore, the porphyrin macrocycle system cannot be utilized simultaneously as the binding moiety as well as the reporting moiety for the formation of fluorescence "turn-on" Zn^{2+} probes.[146] Fortunately, its *meso*-positions can be readily modified with different functionalization, and thus Lippard *et al.* synthesized Zn^{2+} probes by incorporating dipicolylamine (DPA) moieties as the binding motifs.[147] Wang, Lv and co-workers developed a ratiometric fluorescent Zn^{2+} probe by the combination of a triamino Zn^{2+} chelating unit with a porphyrin fluorophore.[148] The triamino unit exhibit good Zn^{2+} affinity and enhanced water solubility of the probe. Ye *et al.* developed two fluorescent Cu^{2+} probes, which emit red fluorescence using a zinc porphyrin as the fluorophore and 2,2′-dipyridylamine (DPA) as the receptor site[149,150] in $CHCl_3$. Porphyrin analogues can be effectively synthesized by replacing one of the pyrrole units with a 1,3-phenylene moiety resulting in a N_3C cavity for Zn^{2+} sensing. Hung *et al.* synthesized an oligopyrrole compound in one pot with a yield of 27%, and reported as a fluorescent probe for sensing Zn^{2+}.[151] The presence of a relatively flexible conjugation framework renders no apparent fluorescence in acetonitrile. But the fluorescence at 672 nm was sharply enhanced upon addition of Zn^{2+}, (The probe shows sufficient selectivity towards Zn^{2+}, with appreciable interference from Cd^{2+} and Hg^{2+} only). The Zn^{2+} sensing procedure was monitored by mass spectrum, NMR, Job's plot and X-ray analysis, which clearly indicated the formation of a zinc complex of with a Zn^{2+}/ stoichiometry of 1 : 1.

Many approaches have been explored to enhance the performance of fluorescent sensors for zinc ion detection.[126,115,152,153] Recently, Xia *et. al.* reported the synthesis of borondipyrromethene (BODIPY) based sensors and their application in monitoring Zn^{2+} in solution and living cells with high selectivity and sensitivity over other competitive metal ions.[126] Photochromic fluorescence chemosensor for Zn^{2+} based on diarylethene linked with Schiff base derivative has also been reported, lately.[141] Fluorescent sensor for Al^{3+} and Zn^{2+} based on europium complex with a 1,10 phenanthroline ligand [135] and for Cd^{2+} and Zn^{2+} based on diarylethene with a pyrine unit.[136] Colorimetric sensors based on silver nanoparticles for Cd^{2+}, Hg^{2+} and Pb^{2+} ions and nanoparticles functionalized for metal ions were reported.[128,154]

Several fluorescent and colorimetric sensors for $Hg^{2+}$and Cd^{2+} ions have been reported in the literature.[155,156] Mostly developed sensors suffer from poor sensing properties including sensitivity and selectivity, high light scattering, low binding affinities. Reports on colorimetric hydrogel based sensors for detection of heavy metal ions in an aqueous medium with satisfactory comprehensive performance are scarce. For instance, a novel hydrophilic colorimetric sensor which could easily detect spectroscopically silent zinc, cadmium and mercury ions in water and cells. As these metal ions because of their closed-shell electronic configuration shows neither magnetic nor spectroscopic signal.[120,157] It has been observed that the colorimetric solid sensors render a robust way for sensing and quantification of metal ions with high selectivity and sensitivity. Visual detection is an increasingly attractive method in various fields because both qualitative and semi-qualitative analyses can be performed without any advanced or complicated instrumentation. It is most useful for the rapid diagnostics in disaster situations where low cost, rapidity and simplicity is required.

Sensing of group 12 metals: Owing to their biological importance or environmental harm, zinc, cadmium, and mercury, have attracted more and more attention. However, selective identification of zinc, cadmium, and mercury ions has always been challenging mainly because of their closed-shell d^{10} electronic configurations making them to be spectroscopically silent. Fluorescent sensors because of its high sensitivity and simplicity as well as ease of signal transduction have thus become the most effective means for detecting the metal ions.[158] Although there are many fluorescent sensors developed for zinc (II),[159] cadmium (II),[160] or mercury(II),[161] but few sensors have been reported which can detect the three cations simultaneously.[162] Instead, there still exist some inadequacy among the known chemosensor: limited fluorophores are there for detecting the cations; most of the sensors exhibit fluorescence quenching; and have relatively scarce “turn-on” responses, and usually the detections are carried out in non-polar or organic solvents which limited practical applications of many sensors.[163] So, development of new turn-on fluorescent chemosensors and colorimetric sensors for the selective detection of under aqueous conditions is still practical and challenging.

The detection of group 12 metal ions is perplexing and problematic because they are spectroscopically and magnetically inactive due to its d^{10} electronic configuration. The presence of the d^{10} electronic configuration resists the application of the analytical techniques such as EPR spectroscopy, Mossbauer, and magnetic susceptibility measurements for their recognition.[164] On the other hand, fluorescence spectroscopy or emission spectroscopy can be fruitfully applied for group 12 metal cations because their metal complexes change the fluorescence intensity of organic fluorophores having coordinated center.[165-167] metal ions [d^{10}] lead to diverse complex nuclearity, which may be explained by the fifty years old hard and soft acids and bases (HSAB) principle.[168] This principle becomes the guiding line of structural diversity of d^{10} metal coordination complexes.

A new fluorescent chemosensor, which shows enhanced fluorescent responses in the presence of Zn^{2+}, Cd^{2+}, and Hg^{2+} and could also simultaneously and selectively differentiate the three cations in a simulated physiological condition. This sensor is based on a helical imide as fluorophore and a cyclen moiety as ionophore with the help of cysteine as an auxiliary reagent.[158]

1.7.7 Elimination of heavy metals

Heavy metal ions are usually removed physically and chemically from the wastewater via conventional process such as coagulation/ flocculation, reverse osmosis, complexation/sequestration, electrochemical operation, ion exchange, biological treatment, chemical precipitation, adsorption, membrane filtration, zeolites, carbon-based sorbent. The above mentioned process becomes economically non-viable for the removal of heavy metals at lower concentrations and may cause secondary contamination.[169-171] Several techniques have been developed to eliminate heavy metal ions from wastewater but each one exhibits limitations for instance in case of solvent extraction the eluent has to be processed to avoid any further pollution. Chemical precipitation of toxic sediments is not an economically successful method, then regarding adsorption of pollutants on solid sorbents appeared to be an efficient technique. Among all these adsorption techniques is widely regarded as an easy, effective and versatile method for the removal of heavy metals from aqueous solution. The high-water retention capacity of hydrogel allows more rapid ion penetration into the cross-linked framework of hydrogel.[172] They undergo reversible change in volume towards external stimuli such as change in pH and temperature. This property brought about the utilization of hydrogels as molecular detectors, absorbent, and sensors. The highly porous structure of hydrogel allows water molecules, ions to easily diffuse and interact with functional groups (-COOH, -NH_2, -OH) in a polymeric network. The potential of hydrogels to be complex with metal ions allows them to be an efficient metal absorbent.[173] Depending on the type of the polymers used, as well as on the properties, nature and density of the network junctions, such structures are in an equilibrium with aqueous medium can contain different amounts of water with a low optical background, high loading capacity, and good biocompatibility. Hydrogels which can swell up to thousands of times of their dry mass in aqueous media in response to external stimuli are called smart materials. This is due to the presence of hydrophilic functional groups like -NH_2,

–OH, -COOH, and -SO_3H in the three dimensional structures, these groups can interact with pollutant species through both electrostatic and secondary interactions in aqueous media.[174] Hydrogels are perfect for optical sensor immobilization owing good biocompatibility, better sensor loading capacity, and very low optical background.[175] Further, by mixing with different monomers hydrogel backbone property such as charge and hydrophobicity can be modified, allowing control of sensor performance.

Various other methods have been reported to remove toxic metal ions from water for instance, Cerium phosphate polypyrrole flower like nanocomposite material ($CePO_4$-PPY) was found to be a promising adsorbent for the efficient removal of Cr (VI) from wastewater. The removal process involved both adsorption and simultaneous in situ chemical reduction of Cr (VI) and to Cr (III).[176] Nanocomposite based on Lanthanum phosphate polyaniline ($LaPO_4$-PANI) was found to be promising adsorbent for the removal of Cr (VI). The adsorption mechanism involved combined effect of both adsorption and reduction.[176] The core–shell nanocomposite based on polyaniline (PANI) and thorium dioxide (ThO_2) used for the removal of Cr (VI) from water. ThO_2-PANI nanocomposite could effectively adsorb Cr (VI) and partially reduced to Cr (III) during the adsorption experiment.[177] Adsorbent based on lanthanum phosphate (LaP) and poly o-toluidine (POT) was found to be effective adsorbent with higher regeneration capability and potential removal of fluoride from ground contaminated water.[178] Table 1. Showing few reported hydrogels-based adsorbent with removal efficiency.

Methods for the removal of Zn^{2+}, Cd^{2+} and Hg^{2+} from water have been reported. For instance, DNA-functionalized polyacrylamide hydrogels employed for Hg^{2+}removal from water.[179] A modified mesoporous conjugate adsorbent was formulated by fixing the organic ligand of 2-hydroxyacetophenone-4 N-pyrrolidine thiosemicarbazones onto mesoporous ZSM-5 for selective and effective mercury removal from aqueous solution.[156] Highly ordered mesoporous silica impregnated with ligand N, N-disalicylidene-4,5- dimethyl-phenylenedene based optical nanocomposite material used for the sensitive and selective removal of $Hg^{2+}$from waste water.[180] Mesoporous silver-melamine based nanocomposites formulated by controlled supramolecular self-assembly employed for selective removal Hg^{2+}.[155] Poly(N-isopropylacrylamide) hydrogel cross-linked with the diacryloyl derivative of cysteine used for removal of Cd^{2+} and Pb^{2+}.[172] A sensitive fluorescent sensor i.e. 2,2-dipicolylamine modified naphthalimide fluorophore followed by immobilization to the surface of silica microsphere used for detection and removal of Cd^{2+}, Hg^{2+} and Pb^{2+} toxic metal ions from aqueous samples.[181] Red mud, waste of an aluminium industry has been transformed into an efficient and inexpensive adsorbent for Zn^{2+}, Cd^{2+} .[182] Carbon aerogel is a new form of activated carbon used for adsorption Pb^{2+}, Cd^{2+} and Hg^{2+} metal ions.[183] Rice straw was used as a bio-sorbent for adsorption of Cu^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+} ions in industrial effluents.[184]

Table 1.1 Showing Adsorption capacity and percentage removal of various heavy metal ions by hydrogel based adsorbents.

S. No	Hydrogel based Adsorbents	Adsorption Capacity $q_e(mg/g)$	% Removal	References
1.	Spherical chitosan/gelatin hydrogel particles	Hg^{2+} 47.5, Pb^{2+} 7.62, Cd^{2+} 0, Cr^{3+} 1.5	Hg^{2+} 84.7, Pb^{2+} 8.7, Cd^{2+} 0, Cr^{3+} 6.7	185
2.	Spherical shaped graphene oxide incorporated chitosan-gelatin hydrogel particles	Hg^{2+} 54.6, Pb^{2+} 5.4, Cd^{2+} 1.67, Cr^{3+} 0	Hg^{2+} 54.6, Pb^{2+} 7.3, Cd^{2+} 1.9, Cr^{3+} 0	186

3.	Poly (acrylamide-co-sodium methacrylate) based hydrogel	Cu^{2+} 24.05, Cd^{2+} 33.0	Cu^{2+} 48, Cd^{2+} 66	187
4.	Polyacrylamide based hydrogel	Cd^{2+} 5.3 mmol. g^{-1}, Pb^{2+} 0.63 mmol. g^{-1}, Zn^{2+} 1.27 mmol. g^{-1}		188
5.	Polyacrylic acid hydrogel	Cd^{2+} 132.9, Cr^{6+} 58.1, Fe^{3+} 12.4, Mn^{2+} 120.4, Ni^{2+} 128.8, Ag^{+} and Ce^{3+} 203.5, Zn^{2+} 157.8	Cd^{2+} 57.1, Cr^{6+} 26.9, Fe^{3+} 5.3, Mn^{2+} 52.7, Ni^{2+} 52.5, Ag^{+} 45.3, Ce^{3+} 70, Zn^{2+} 58.4	189
6.	Gelatin/chitosan hydrogel		Hg^{2+} 97, Pb^{2+} 12, Cd^{2+} 2, Cr^{3+} 24	173
7.	Sulfonic acid based hydrogels	Cd^{2+} 0.95, Cu^{2+} 0.87, Fe^{3+} 0.83, Zn^{2+} 1.00, Mn^{2+} 0.77, Pb^{2+} 0.18		190
8.	Alginate-fibroid hydrogel	Cu^{2+} 316.0, Cd^{2+} 232.35, Pb^{2+} 465.2		191

9.	Graphene oxide/alginate based hydrogel membrane	Pb^{2+} 327.9, Cr^{3+} 118.6		192

1.8 References

(1) Ahmed, E. M.; Aggor, F. S.; Awad, A. M.; El-Aref, A. T. An Innovative Method for Preparation of Nanometal Hydroxide Superabsorbent Hydrogel. Carbohydr. Polym. 2013, 91 (2), 693–698. https://doi.org/10.1016/j.carbpol.2012.08.056.

(2) Ahmed, E. M. Hydrogel: Preparation, Characterization, and Applications: A Review. J. Adv. Res. 2015, 6 (2), 105–121. https://doi.org/10.1016/j.jare.2013.07.006.

(3) Mishra, S.; Rani, P.; Sen, G.; Dey, K. P. Preparation, Properties and Application of Hydrogels: A Review; Springer Singapore, 2018. https://doi.org/10.1007/978-981-10-6077-9_6.

(4) Li, Y.; Huang, G.; Zhang, X.; Li, B.; Chen, Y.; Lu, T.; Lu, T. J.; Xu, F. Magnetic Hydrogels and Their Potential Biomedical Applications. Adv. Funct. Mater. 2013, 23 (6), 660–672. https://doi.org/10.1002/adfm.201201708.

(5) Ali, M.; Husain, Q. Guar Gum Blended Alginate/Agarose Hydrogel as a Promising Support for the Entrapment of Peroxidase: Stability and Reusability Studies for the Treatment of Textile Effluent. Int. J. Biol. Macromol. 2018, 116, 463–471. https://doi.org/10.1016/j.ijbiomac.2018.05.037.

(6) Burkert, S.; Schmidt, T.; Gohs, U.; Dorschner, H.; Arndt, K. F. Cross-Linking of Poly(N-Vinyl Pyrrolidone) Films by Electron Beam Irradiation. Radiat. Phys. Chem. 2007, 76 (8–9), 1324–1328. https://doi.org/10.1016/j.radphyschem.2007.02.024.

(7) Ahmad, S.; Ahmad, M.; Manzoor, K.; Purwar, R.; Ikram, S. A Review on Latest

Innovations in Natural Gums Based Hydrogels: Preparations & Applications. Int. J. Biol. Macromol. 2019, 136, 870–890. https://doi.org/10.1016/j.ijbiomac.2019.06.113.

(8) Saravanan, S.; Vimalraj, S.; Thanikaivelan, P.; Banudevi, S.; Manivasagam, G. A Review on Injectable Chitosan/Beta Glycerophosphate Hydrogels for Bone Tissue Regeneration. Int. J. Biol. Macromol. 2019, 121, 38–54. https://doi.org/10.1016/j.ijbiomac.2018.10.014.

(9) Graham, S.; Marina, P. F.; Blencowe, A. Thermoresponsive Polysaccharides and Their Thermoreversible Physical Hydrogel Networks. Carbohydr. Polym. 2019, 207, 143–159. https://doi.org/10.1016/j.carbpol.2018.11.053.

(10) Jonker, A. M.; Löwik, D. W. P. M.; Van Hest, J. C. M. Peptide- and Protein-Based Hydrogels. Chem. Mater. 2012, 24 (5), 759–773. https://doi.org/10.1021/cm202640w.

(11) Mogoşanu, G. D.; Grumezescu, A. M. Natural and Synthetic Polymers for Wounds and Burns Dressing. Int. J. Pharm. 2014, 463 (2), 127–136. https://doi.org/10.1016/j.ijpharm.2013.12.015.

(12) Buwalda, S. J.; Boere, K. W. M.; Dijkstra, P. J.; Feijen, J.; Vermonden, T.; Hennink, W. E. Hydrogels in a Historical Perspective: From Simple Networks to Smart Materials. J. Control. Release 2014, 190, 254–273. https://doi.org/10.1016/j.jconrel.2014.03.052.

(13) Vermonden, T.; Klumperman, B. The Past, Present and Future of Hydrogels. Eur. Polym. J. 2015, 72 , 341–343. https://doi.org/10.1016/j.eurpolymj.2015.08.032.

(14) Ikram, S.; Kumari, M.; Gupta, B. Thermosensitive Membranes by Radiation-Induced Graft Polymerization of N-Isopropyl Acrylamide/Acrylic Acid on Polypropylene Nonwoven Fabric. Radiat. Phys. Chem. 2011, 80 (1), 50–56. https://doi.org/10.1016/j.radphyschem.2010.08.013.

(15) Noreen, A.; Nazli, Z. i. H.; Akram, J.; Rasul, I.; Mansha, A.; Yaqoob, N.; Iqbal, R.;

Tabasum, S.; Zuber, M.; Zia, K. M. Pectins Functionalized Biomaterials; a New Viable Approach for Biomedical Applications: A Review. Int. J. Biol. Macromol. 2017, 101, 254–272. https://doi.org/10.1016/j.ijbiomac.2017.03.029.

(16) Yang, Z.; Peng, H.; Wang, W.; Liu, T. Crystallization Behavior of Poly(ε-Caprolactone)/Layered Double Hydroxide Nanocomposites. J. Appl. Polym. Sci. 2010, 116 (5), 2658–2667. https://doi.org/10.1002/app.

(17) Yang, L.; Chu, J. S.; Fix, J. A. Colon-Specific Drug Delivery: New Approaches and in Vitro/in Vivo Evaluation. Int. J. Pharm. 2002, 235 (1–2), 1–15. https://doi.org/10.1016/S0378-5173(02)00004-2.

(18) Maolin, Z.; Jun, L.; Min, Y.; Hongfei, H. The Swelling Behavior of Radiation Prepared Semi-Interpenetrating Polymer Networks Composed of PolyNIPAAm and Hydrophilic Polymers. Radiat. Phys. Chem. 2000, 58 (4), 397–400. https://doi.org/10.1016/S0969-806X(99)00491-0.

(19) Zhang, J. T.; Bhat, R.; Jandt, K. D. Temperature-Sensitive PVA/PNIPAAm Semi-IPN Hydrogels with Enhanced Responsive Properties. Acta Biomater. 2009, 5 (1), 488–497. https://doi.org/10.1016/j.actbio.2008.06.012.

(20) Lin, C. C.; Metters, A. T. Hydrogels in Controlled Release Formulations: Network Design and Mathematical Modeling. Adv. Drug Deliv. Rev. 2006, 58 (12–13), 1379–1408. https://doi.org/10.1016/j.addr.2006.09.004.

(21) Peppas, N. A.; Hilt, J. Z.; Khademhosseini, A.; Langer, R. Hydrogels in Biology and Medicine: From Molecular Principles to Bionanotechnology. Adv. Mater. 2006, 18 (11), 1345–1360. https://doi.org/10.1002/adma.200501612.

(22) Tønnesen, H. H.; Karlsen, J. Alginate in Drug Delivery Systems. Drug Dev. Ind. Pharm.

2002, 28 (6), 621–630. https://doi.org/10.1081/DDC-120003853.

(23) Xian, C.; Yuan, Q.; Bao, Z.; Liu, G.; Wu, J. Progress on Intelligent Hydrogels Based on RAFT Polymerization: Design Strategy, Fabrication and the Applications for Controlled Drug Delivery. Chinese Chem. Lett. 2020, 31 (1), 19–27. https://doi.org/10.1016/j.cclet.2019.03.052.

(24) Carter, P.; Narasimhan, B.; Wang, Q. Biocompatible Nanoparticles and Vesicular Systems in Transdermal Drug Delivery for Various Skin Diseases. Int. J. Pharm. 2019, 555, 49–62. https://doi.org/10.1016/j.ijpharm.2018.11.032.

(25) Wei, X.; Liao, J.; Davoudi, Z.; Zheng, H.; Chen, J.; Li, D.; Xiong, X.; Yin, Y.; Yu, X.; Xiong, J.; Wang, Q. Folate Receptor-Targeted and Gsh-Responsive Carboxymethyl Chitosan Nanoparticles Containing Covalently Entrapped 6-Mercaptopurine for Enhanced Intracellular Drug Delivery in Leukemia. Mar. Drugs 2018, 16 (11). https://doi.org/10.3390/md16110439.

(26) Li, Z.; Ramay, H. R.; Hauch, K. D.; Xiao, D.; Zhang, M. Chitosan-Alginate Hybrid Scaffolds for Bone Tissue Engineering. Biomaterials 2005, 26 (18), 3919–3928. https://doi.org/10.1016/j.biomaterials.2004.09.062.

(27) Huang, K.; Wu, J.; Gu, Z. Black Phosphorus Hydrogel Scaffolds Enhance Bone Regeneration via a Sustained Supply of Calcium-Free Phosphorus. ACS Appl. Mater. Interfaces 2019, 11 (3), 2908–2916. https://doi.org/10.1021/acsami.8b21179.

(28) Brown, J. Q.; Srivastava, R.; McShane, M. J. Encapsulation of Glucose Oxidase and an Oxygen-Quenched Fluorophore in Polyelectrolyte-Coated Calcium Alginate Microspheres as Optical Glucose Sensor Systems. Biosens. Bioelectron. 2005, 21 (1), 212–216. https://doi.org/10.1016/j.bios.2004.08.020.

(29) Whitchurch, C. B.; Alm, R. A.; Mattick, J. S. The Alginate Regulator AlgR and an

Associated Sensor FimS Are Required for Twitching Motility in Pseudomonas Aeruginosa. Proc. Natl. Acad. Sci. U. S. A. 1996, 93 (18), 9839–9843. https://doi.org/10.1073/pnas.93.18.9839.

(30) Lum, E.; Golebiowski, B.; Gunn, R.; Babhoota, M.; Swarbrick, H. Corneal Sensitivity with Contact Lenses of Different Mechanical Properties. Optom. Vis. Sci. 2013, 90 (9), 954–960. https://doi.org/10.1097/OPX.0000000000000016.

(31) Lee, K. Y.; Mooney, D. J. Hydrogels for Tissue Engineering. Chem. Rev. 2001, 101 (7), 1869–1879. https://doi.org/10.1021/cr000108x.

(32) Loh, Q. L.; Choong, C. Three-Dimensional Scaffolds for Tissue Engineering Applications: Role of Porosity and Pore Size. Tissue Eng. - Part B Rev. 2013, 19 (6), 485–502. https://doi.org/10.1089/ten.teb.2012.0437.

(33) Ma, P. X. Scaffolds for Tissue Fabrication. Mater. Today 2004, 7 (5), 30–40. https://doi.org/10.1016/S1369-7021(04)00233-0.

(34) Sloff, M.; Simaioforidis, V.; De Vries, R.; Oosterwijk, E.; Feitz, W. Tissue Engineering of the Bladder - Reality or Myth? A Systematic Review. J. Urol. 2014, 192 (4), 1035–1042. https://doi.org/10.1016/j.juro.2014.03.116.

(35) Makris, E. A.; Gomoll, A. H.; Malizos, K. N.; Hu, J. C.; Athanasiou, K. A. Repair and Tissue Engineering Techniques for Articular Cartilage. Nat. Rev. Rheumatol. 2015, 11 (1), 21–34. https://doi.org/10.1038/nrrheum.2014.157.

(36) Naahidi, S.; Jafari, M.; Logan, M.; Wang, Y.; Yuan, Y.; Bae, H.; Dixon, B.; Chen, P. Biocompatibility of Hydrogel-Based Scaffolds for Tissue Engineering Applications. Biotechnol. Adv. 2017, 35 (5), 530–544. https://doi.org/10.1016/j.biotechadv.2017.05.006.

(37) Jeong, K. H.; Park, D.; Lee, Y. C. Polymer-Based Hydrogel Scaffolds for Skin Tissue

Engineering Applications: A Mini-Review. J. Polym. Res. 2017, 24 (7). https://doi.org/10.1007/s10965-017-1278-4.

(38) Liu, Y.; Lim, J.; Teoh, S. H. Review: Development of Clinically Relevant Scaffolds for Vascularised Bone Tissue Engineering. Biotechnol. Adv. 2013, 31 (5), 688–705. https://doi.org/10.1016/j.biotechadv.2012.10.003.

(39) Purwar, R.; Rajput, P.; Srivastava, C. M. Composite Wound Dressing for Drug Release. Fibers Polym. 2014, 15 (7), 1422–1428. https://doi.org/10.1007/s12221-014-1422-2.

(40) Fonder, M. A.; Lazarus, G. S.; Cowan, D. A.; Aronson-Cook, B.; Kohli, A. R.; Mamelak, A. J. Treating the Chronic Wound: A Practical Approach to the Care of Nonhealing Wounds and Wound Care Dressings. J. Am. Acad. Dermatol. 2008, 58 (2), 185–206. https://doi.org/10.1016/j.jaad.2007.08.048.

(41) Cuttle, L.; Pearn, J.; McMillan, J. R.; Kimble, R. M. A Review of First Aid Treatments for Burn Injuries. Burns 2009, 35 (6), 768–775. https://doi.org/10.1016/j.burns.2008.10.011.

(42) Coats, T. J.; Edwards, C.; Newton, R.; Staun, E. The Effect of Gel Burns Dressings on Skin Temperature. Emerg. Med. J. 2002, 19 (3), 224–225. https://doi.org/10.1136/emj.19.3.224.

(43) Grippaudo, F. R.; Carini, L.; Baldini, R. Procutase® versus 1% Silver Sulphadiazine in the Treatment of Minor Burns. Burns 2010, 36 (6), 871–875. https://doi.org/10.1016/j.burns.2009.10.021.

(44) Shahid, S. A.; Qidwai, A. A.; Anwar, F.; Ullah, I.; Rashid, U. Effects of a Novel Poly (AA-Co-AAm)/AlZnFe 2O 4/ Potassium Humate Superabsorbent Hydrogel Nanocomposite on Water Retention of Sandy Loam Soil and Wheat Seedling Growth. Molecules 2012, 17 (11), 12587–12602. https://doi.org/10.3390/molecules171112587.

(45) Silberbush, M.; Adar, E.; De Malach, Y. Use of an Hydrophilic Polymer to Improve Water Storage and Availability to Crops Grown in Sand Dunes I. Corn Irrigated by Trickling. Agric. Water Manag. 1993, 23 (4), 303–313. https://doi.org/10.1016/0378-3774(93)90042-9.

(46) Zonatto, F.; Muniz, E. C.; Tambourgi, E. B.; Paulino, A. T. Adsorption and Controlled Release of Potassium, Phosphate and Ammonia from Modified Arabic Gum-Based Hydrogel. Int. J. Biol. Macromol. 2017, 105, 363–369. https://doi.org/10.1016/j.ijbiomac.2017.07.051.

(47) Du, H.; Shi, S.; Liu, W.; Teng, H.; Piao, M. Processing and Modification of Hydrogel and Its Application in Emerging Contaminant Adsorption and in Catalyst Immobilization: A Review. Environ. Sci. Pollut. Res. 2020, 27 (12), 12967–12994. https://doi.org/10.1007/s11356-020-08096-6.

(48) Ahmad, M.; Manzoor, K.; Chaudhuri, R. R.; Ikram, S. Thiocarbohydrazide Cross-Linked Oxidized Chitosan and Poly(Vinyl Alcohol): A Green Framework as Efficient Cu(II), Pb(II), and Hg(II) Adsorbent. J. Chem. Eng. Data 2017, 62 (7), 2044–2055. https://doi.org/10.1021/acs.jced.7b00088.

(49) Ahmad, M.; Ahmed, S.; Swami, B. L.; Ikram, S. Preparation and Characterization of Antibacterial Thiosemicarbazide Chitosan as Efficient Cu(II) Adsorbent. Carbohydr. Polym. 2015, 132 (Ii), 164–172. https://doi.org/10.1016/j.carbpol.2015.06.034.

(50) Oussalah, A.; Boukerroui, A.; Aichour, A.; Djellouli, B. Cationic and Anionic Dyes Removal by Low-Cost Hybrid Alginate/Natural Bentonite Composite Beads: Adsorption and Reusability Studies. Int. J. Biol. Macromol. 2019, 124, 854–862. https://doi.org/10.1016/j.ijbiomac.2018.11.197.

(51) Sharma, G.; Kumar, A.; Naushad, M.; García-Peñas, A.; Al-Muhtaseb, A. H.; Ghfar, A. A.; Sharma, V.; Ahamad, T.; Stadler, F. J. Fabrication and Characterization of Gum Arabic-Cl-Poly(Acrylamide) Nanohydrogel for Effective Adsorption of Crystal Violet Dye.

Carbohydr. Polym. 2018, 202, 444–453. https://doi.org/10.1016/j.carbpol.2018.09.004.

(52) Naushad, M.; Sharma, G.; Kumar, A.; Sharma, S.; Ghfar, A. A.; Bhatnagar, A.; Stadler, F. J.; Khan, M. R. Efficient Removal of Toxic Phosphate Anions from Aqueous Environment Using Pectin Based Quaternary Amino Anion Exchanger. Int. J. Biol. Macromol. 2018, 106, 1–10. https://doi.org/10.1016/j.ijbiomac.2017.07.169.

(53) Hoare, T. R.; Kohane, D. S. Hydrogels in Drug Delivery: Progress and Challenges. Polymer (Guildf). 2008, 49 (8), 1993–2007. https://doi.org/10.1016/j.polymer.2008.01.027.

(54) Chiang, W. H.; Ho, V. T.; Huang, W. C.; Huang, Y. F.; Chern, C. S.; Chiu, H. C. Dual Stimuli-Responsive Polymeric Hollow Nanogels Designed as Carriers for Intracellular Triggered Drug Release. Langmuir 2012, 28 (42), 15056–15064. https://doi.org/10.1021/la302903v.

(55) Oishi, M.; Nagasaki, Y. Stimuli-Responsive Smart Nanogels for Cancer Diagnostics and Therapy. Nanomedicine 2010, 5 (3), 451–468. https://doi.org/10.2217/nnm.10.18.

(56) Shariatinia, Z.; Jalali, A. M. Chitosan-Based Hydrogels: Preparation, Properties and Applications. Int. J. Biol. Macromol. 2018, 115, 194–220. https://doi.org/10.1016/j.ijbiomac.2018.04.034.

(57) Ullah, F.; Othman, M. B. H.; Javed, F.; Ahmad, Z.; Akil, H. M. Classification, Processing and Application of Hydrogels: A Review. Mater. Sci. Eng. C 2015, 57, 414–433. https://doi.org/10.1016/j.msec.2015.07.053.

(58) Khan, M.; Lo, I. M. C. A Holistic Review of Hydrogel Applications in the Adsorptive Removal of Aqueous Pollutants: Recent Progress, Challenges, and Perspectives. Water Res. 2016, 106, 259–271. https://doi.org/10.1016/j.watres.2016.10.008.

(59) Qi, X.; Li, Z.; Shen, L.; Qin, T.; Qian, Y.; Zhao, S.; Liu, M.; Zeng, Q.; Shen, J. Highly

Efficient Dye Decontamination via Microbial Salecan Polysaccharide-Based Gels. Carbohydr. Polym. 2019, 219 (January), 1–11. https://doi.org/10.1016/j.carbpol.2019.05.021.

(60) Tang, S. C. N.; Wang, P.; Yin, K.; Lo, I. M. C. Synthesis and Application of Magnetic Hydrogel for Cr(VI) Removal from Contaminated Water. Environ. Eng. Sci. 2010, 27 (11), 947–954. https://doi.org/10.1089/ees.2010.0112.

(61) Shah, L. A.; Khan, M.; Javed, R.; Sayed, M.; Khan, M. S.; Khan, A.; Ullah, M. Superabsorbent Polymer Hydrogels with Good Thermal and Mechanical Properties for Removal of Selected Heavy Metal Ions. J. Clean. Prod. 2018, 201, 78–87. https://doi.org/10.1016/j.jclepro.2018.08.035.

(62) Thompson, B. R.; Horozov, T. S.; Stoyanov, S. D.; Paunov, V. N. Hierarchically Porous Composites Fabricated by Hydrogel Templating and Viscous Trapping Techniques. Mater. Des. 2018, 137, 384–393. https://doi.org/10.1016/j.matdes.2017.10.046.

(63) Afzal, M. Z.; Yue, R.; Sun, X. F.; Song, C.; Wang, S. G. Enhanced Removal of Ciprofloxacin Using Humic Acid Modified Hydrogel Beads. J. Colloid Interface Sci. 2019, 543, 76–83. https://doi.org/10.1016/j.jcis.2019.01.083.

(64) Kluczka, J.; Gnus, M.; Kazek-Kęsik, A.; Dudek, G. Zirconium-Chitosan Hydrogel Beads for Removal of Boron from Aqueous Solutions. Polymer (Guildf). 2018, 150, 109–118. https://doi.org/10.1016/j.polymer.2018.07.010.

(65) Bilal, M.; Jing, Z.; Zhao, Y.; Iqbal, H. M. N. Immobilization of Fungal Laccase on Glutaraldehyde Cross-Linked Chitosan Beads and Its Bio-Catalytic Potential to Degrade Bisphenol A. Biocatal. Agric. Biotechnol. 2019, 19 (March). https://doi.org/10.1016/j.bcab.2019.101174.

(66) Gogoi, N.; Barooah, M.; Majumdar, G.; Chowdhury, D. Carbon Dots Rooted Agarose

Hydrogel Hybrid Platform for Optical Detection and Separation of Heavy Metal Ions. ACS Appl. Mater. Interfaces 2015, 7 (5), 3058–3067. https://doi.org/10.1021/am506558d.

(67) Yin, S.; Ma, Z. “Smart” Sensing Interface for the Improvement of Electrochemical Immunosensor Based on Enzyme-Fenton Reaction Triggered Destruction of Fe3+ Cross-Linked Alginate Hydrogel. Sensors Actuators, B Chem. 2019, 281 (May 2018), 857–863. https://doi.org/10.1016/j.snb.2018.11.030.

(68) Zhang, C.; Li, H.; Yu, Q.; Jia, L.; Wan, L. Y. Poly(Aspartic Acid) Electrospun Nanofiber Hydrogel Membrane-Based Reusable Colorimetric Sensor for Cu(II) and Fe(III) Detection. ACS Omega 2019. https://doi.org/10.1021/acsomega.9b02109.

(69) Zhang, W.; Cheng, W.; Ziemann, E.; Be’er, A.; Lu, X.; Elimelech, M.; Bernstein, R. Functionalization of Ultrafiltration Membrane with Polyampholyte Hydrogel and Graphene Oxide to Achieve Dual Antifouling and Antibacterial Properties. J. Memb. Sci. 2018, 565, 293–302. https://doi.org/10.1016/j.memsci.2018.08.017.

(70) Wang, H.; Liu, Z. hua; Zhang, J.; Huang, R. ping; Yin, H.; Dang, Z.; Wu, P. xiao; Liu, Y. Insights into Removal Mechanisms of Bisphenol A and Its Analogues in Municipal Wastewater Treatment Plants. Sci. Total Environ. 2019, 692, 107–116. https://doi.org/10.1016/j.scitotenv.2019.07.134.

(71) Zhao, L.; Deng, J.; Sun, P.; Liu, J.; Ji, Y.; Nakada, N.; Qiao, Z.; Tanaka, H.; Yang, Y. Nanomaterials for Treating Emerging Contaminants in Water by Adsorption and Photocatalysis: Systematic Review and Bibliometric Analysis. Sci. Total Environ. 2018, 627, 1253–1263. https://doi.org/10.1016/j.scitotenv.2018.02.006.

(72) Zhang, C.; Li, H.; Yu, Q.; JLA, L.; Wan, LY. Poly (aspartic acid) Electrospun Nanofiber Hydrogel Membrane-Based Reusable Colorimetric Sensor for Cu(II) and Fe(III) Detection. ACS Omega. 2019 4 (11), 14633-14639 DOI: 10.1021/acsomega.9b02109

(73) Büning, D.; Roth,FE.; Walter,SV.; Hennecke, T.; Ulbricht,M. Potassium-sensitive poly(N-isopropylacrylamide)-based hydrogels for sensor applications. Polym. Chem. 2018 ,9, 3600-3614 https://doi.org/10.1039/C8PY00490K

(74) Ozay, H.; Ozay, O. Rhodamine based reusable and colorimetric naked-eye hydrogel sensors for Fe3+ ion. Chemical Engineering Journal. 2013, 232,364-371, https://doi.org/10.1016/j.cej.2013.07.111.

(75) Joseph, KA.; Dave, N.; Liu, J. Electrostatically Directed Visual Fluorescence Response of DNA-Functionalized Monolithic Hydrogels for Highly Sensitive Hg2+ Detection. ACS Applied Materials & Interfaces. 2011 3 (3), 733-739 DOI: 10.1021/am101068c

(76) Tasneam, K.; El-damhougy, Amal, S.I.;Ahmed, Ghalia A;. Gaber, Nabila A.; Mazied, Ghada Bassioni,; Radiation synthesis for a highly sensitive colorimetric hydrogel sensor-based p(AAc/AMPS)-TA for metal ion detection. Results in Materials. 2021, 9, 100169, ISSN 2590-048X, https://doi.org/10.1016/j.rinma.2021.100169.

(77) Buenger, D.; Topuz, F.; Groll, J.; Hydrogels in sensing applications. Progress in Polymer Science. 2012, 37, (12),2012, 1678-1719, ISSN 0079-6700, https://doi.org/10.1016/j.progpolymsci.2012.09.001.

(78) Sun, X.; Agate,S.; Samaher Salem, K.; Lucia,L.; Pal ,L.; Hydrogel-Based Sensor Networks: Compositions, Properties, and Applications. ACS Applied Bio Materials. 2021, 4 (1), 140-162 DOI: 10.1021/acsabm.0c01011

(79) Hou, W.; Sheng, N.; Zhang, X.; Luan, Z.; Qi, P.; Lin, M.; Tan, Y.; Xia, Y.; Li, Y.; Sui, K. Design of Injectable Agar/NaCl/ Polyacrylamide Ionic Hydrogels for High Performance Strain Sensors. Carbohydr. Polym. 2019, 211, 322−328.

(80) Wu, R.; Zhang, S.; Lyu, J.; Lu, F.; Yue, X.; Lv, J. A Visual Volumetric Hydrogel Sensor Enables Quantitative and Sensitive Detection of Copper Ions. Chem. Commun. 2015, 51 (38), 8078− 8081.

(81) Guo, J.; Zhou, M.; Yang, C. Fluorescent Hydrogel Waveguide for On-Site Detection of Heavy Metal Ions. Sci. Rep. 2017, 7 (1), 7902.

(82) Dave, N.; Chan, M. Y.; Huang, P.-J. J.; Smith, B. D.; Liu, J. Regenerable DNA-Functionalized Hydrogels for Ultrasensitive, Instrument-Free Mercury(II) Detection and Removal in Water. J. Am. Chem. Soc. 2010, 132 (36), 12668−12673.

(83) Ye, B.F.; Zhao, Y.; Yuan-Jin.; Cheng, Y.; Li, T.T.; Xie, ZY.; Zhao, XW.; Gu, Z.Z. Colorimetric photonic hydrogel aptasensor for the screening of heavy metal ions. Nanoscale. 2012, 4(19), 5998-6003, http://dx.doi.org/10.1039/C2NR31601C

(84) Diehl, F.; S, Hageneder.; S, Fossati.; A, Simone K.; J, Dostalek.; U, Jonas. Plasmonic nanomaterials with responsive polymer hydrogels for sensing and actuation. Chem. Soc. Rev. 2022, 51(10), 3926-3963. http://dx.doi.org/10.1039/D1CS01083B",

(85) Kahn, J.S.; Hu, Y.; Willner, I.; Stimuli-Responsive DNA-Based Hydrogels: From Basic Principles to Applications. Accounts of Chemical Research. 2017 50 (4), 680-690 DOI: 10.1021/acs.accounts.6b00542

(86) Hu, J.; Zhang, G.; Liu, S. Enzyme-responsive polymeric assemblies’ nanoparticles and hydrogel.Chem. Soc. Rev. 2012, 41(18) 5933-5949. http://dx.doi.org/10.1039/C2CS35103J.

(87) Heidi R.; John R. C.; Nicholas A. P. Analyte-Responsive Hydrogels: Intelligent Materials for Biosensing and Drug Delivery Accounts of Chemical Research 2017, 50 (2), 170-178. DOI: 10.1021/acs.accounts.6b00533.

(88) Gao, J.; Grady, B. P. Reaction Kinetics and Subsequent Rheology of Carboxymethyl Guar Gum Produced from Guar Splits. Ind. Eng. Chem. Res. 2018, 57 (22), 7345–7354. https://doi.org/10.1021/acs.iecr.8b00782.

(89) Caenn, R.; Chillingar, G. V. Drilling Fluids: State of the Art. J. Pet. Sci. Eng. 1996, 14 (3–4), 221–230. https://doi.org/10.1016/0920-4105(95)00051-8.

(90) Shaikh, T.; Kumar, S. S. AcademicScienceS. 2011, 3, 17–19.

(91) Mudgil, D.; Barak, S.; Khatkar, B. S. Guar Gum: Processing, Properties and Food Applications - A Review. J. Food Sci. Technol. 2014, 51 (3), 409–418. https://doi.org/10.1007/s13197-011-0522-x.

(92) Šostar, S.; Schneider, R. Guar Gum as an Environment-Friendly Alternative Thickener in Printing with Reactive Dyes. Dye. Pigment. 1998, 39 (4), 211–221. https://doi.org/10.1016/S0143-7208(97)00111-3.

(93) Bhardwaj, T. R.; Kanwar, M.; Lal, R. Drug Development and Industrial Pharmacy Natural Gums and Modified Natural Gums as Sustained-Release Carriers. Drug Dev. Ind. Pharm. 2000, 26 (768506750), 1025–1038.

(94) Kumar, M. International Journal of Pharma and Bio Sciences ISSN. Int. J. Pharma Bio Sci. 2015, 6 (3), 679–685.

(95) Mundargi, R. C.; Agnihotri, S. A.; Patil, S. A.; Aminabhavi, T. M. Graft Copolymerization of Methacrylic Acid onto Guar Gum, Using Potassium Persulfate as an Initiator. J. Appl. Polym. Sci. 2006, 101 (1), 618–623. https://doi.org/10.1002/app.23325.

(96) Taunk, K.; Behari, K. Graft Copolymerization of Acrylic Acid onto Guar Gum. J. Appl. Polym. Sci. 2000, 77 (1), 39–44. https://doi.org/10.1002/(sici)1097-4628(20000705)77:1<39::aid-app6>3.0.co;2-z.

(97) Li, X.; Wu, W.; Liu, W. Synthesis and Properties of Thermo-Responsive Guar Gum/Poly(N-Isopropylacrylamide) Interpenetrating Polymer Network Hydrogels. Carbohydr. Polym. 2008, 71 (3), 394–402. https://doi.org/10.1016/j.carbpol.2007.06.005.

(98) Singh, V.; Sharma, A. K.; Maurya, S. Efficient Cadmium(II) Removal from Aqueous Solution Using Microwave Synthesized Guar Gum-Graft-Poly(Ethylacrylate). Ind. Eng. Chem. Res. 2009, 48 (10), 4688–4696. https://doi.org/10.1021/ie801416z.

(99) Singh, V.; Tiwari, A.; Tripathi, D. N.; Sanghi, R. Grafting of Polyacrylonitrile onto Guar Gum under Microwave Irradiation. J. Appl. Polym. Sci. 2004, 92 (3), 1569–1575. https://doi.org/10.1002/app.20099.

(100) Singh, V.; Kumari, P.; Pandey, S.; Narayan, T. Removal of Chromium (VI) Using Poly(Methylacrylate) Functionalized Guar Gum. Bioresour. Technol. 2009, 100 (6), 1977–1982. https://doi.org/10.1016/j.biortech.2008.10.034.

(101) Chowdhury, P.; Samui, S.; Kundu, T.; Nandi, M. M. Graft Polymerization of Methyl Methacrylate onto Guar Gum with Ceric Ammonium Sulfate/Dextrose Redox Pair. J. Appl. Polym. Sci. 2001, 82 (14), 3520–3525. https://doi.org/10.1002/app.2214.

(102) Starnes, S. D.; Arungundram, S.; Saunders, C. H. ChemInform Abstract: Anion Sensors Based on β,B′-Disubstituted Porphyrin Derivatives. ChemInform 2010, 33 (51), no-no. https://doi.org/10.1002/chin.200251131.

(103) Chauhan, D.; Kumar, A.; Warkar, S. G. Synthesis, Characterization and Metal Ions Sensing Applications of Meta-Benziporphodimethene-Embedded Polyacrylamide/Carboxymethyl Guargum Polymeric Hydrogels in Water. Environ. Technol. (United Kingdom) 2020, 0 (0), 1–12. https://doi.org/10.1080/09593330.2020.1812730.

(104) Stępień, M.; Latos-Grazyński, L.; Szterenberg, L.; Panek, J.; Latajka, Z. Cadmium(II)

and Nickel(II) Complexes of Benziporphyrins. A Study of Weak Intramolecular Metal-Arene Interactions. J. Am. Chem. Soc. 2004, 126 (14), 4566–4580. https://doi.org/10.1021/ja039384u.

(105) Hung, C.-H.; Chang, G.-F.; Kumar, A.; Lin, G.-F.; Luo, L.-Y.; Ching, W.-M.; Wei-Guang Diau, E. M-Benziporphodimethene: A New Porphyrin Analogue Fluorescence Zinc(<scp>ii</Scp>) Sensor. Chem. Commun. 2008, No. 8, 978–980. https://doi.org/10.1039/B714412A.

(106) Sharma, R. K.; Gajanan, L. K.; Mehata, M. S.; Hussain, F.; Kumar, A. Synthesis, Characterization and Fluorescence Turn-on Behavior of New Porphyrin Analogue: Meta - Benziporphodimethenes. Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 2016, 169, 58–65. https://doi.org/10.1016/j.saa.2016.06.020.

(107) Ahluwalia, D.; Kumar, A.; Warkar, S. G. Recent Developments in Meta-Benziporphodimethene: A New Porphyrin Analogue. J. Mol. Struct. 2021, 1228, 129672. https://doi.org/10.1016/j.molstruc.2020.129672.

(108) Chang, G. F.; Wang, C. H.; Lu, H. C.; Kan, L. S.; Chao, I.; Chen, W. H.; Kumar, A.; Lo, L.; Dela Rosa, M. A. C.; Hung, C. H. Factors That Regulate the Conformation of M-Benziporphodimethene Complexes: Agostic Metal-Arene Interaction, Hydrogen Bonding, and Î· 2,π Coordination. Chem. - A Eur. J. 2011, 17 (40), 11332–11343. https://doi.org/10.1002/chem.201100780.

(109) Sharma, R. K.; Gajanan, L. K.; Mehata, M. S.; Hussain, F.; Kumar, A. Synthesis, Characterization and Fluorescence Turn-on Behavior of New Porphyrin Analogue: Meta-Benziporphodimethenes. Spectrochim. Acta - Part A Mol. Biomol. Spectrosc. 2016, 169, 58–65. https://doi.org/10.1016/j.saa.2016.06.020.

(110) Chao, Y.-C.; Huang, Y.-S.; Wang, H.-P.; Fu, S.-M.; Huang, C.-H.; Liang, Y.-C.; Yang,

W.-C.; Huang, Y.-S.; Chang, G.-F.; Zan, H.-W.; Meng, H.-F.; Hung, C.-H.; Fu, C.-C. An Organic Hydrogel Film with Micron-Sized Pillar Array for Real-Time and Indicator-Free Detection of Zn2+. Org. Electron. 2011, 12 (11), 1899–1902. https://doi.org/10.1016/j.orgel.2011.07.001.

(111) Andrews, G. K. Cellular Zinc Sensors: MTF-1 Regulation of Gene Expression. BioMetals 2001, 14 (3–4), 223–237. https://doi.org/10.1023/A:1012932712483.

(112) Cuajungco, M. P.; Lees, G. J. Zinc and Alzheimer’s Disease: Is There a Direct Link? Brain Res. Rev. 1997, 23 (3), 219–236. https://doi.org/10.1016/S0165-0173(97)00002-7.

(113) Dexter, D. T.; Carayon, A.; Javoy-agid, F.; Agid, Y.; Wells, F. R.; Daniel, S. E.; Lees, A. J.; Jenner, P.; Marsden, C. D. Alterations in the Levels of Iron, Ferritin and Other Trace Metals in Parkinson’s Disease and Other Neurodegenerative Diseases Affecting the Basal Ganglia. Brain 1991, 114 (4), 1953–1975. https://doi.org/10.1093/brain/114.4.1953.

(114) Murakami, M.; Hirano, T. Intracellular Zinc Homeostasis and Zinc Signaling. Cancer Sci. 2008, 99 (8), 1515–1522. https://doi.org/10.1111/j.1349-7006.2008.00854.x.

(115) Sharma, R. K.; Maurya, A.; Rajamani, P.; Mehata, M. S.; Kumar, A. Meta-Benziporphodimethenes: New Cell-Imaging Porphyrin Analogue Molecules. ChemistrySelect 2016, 1 (13), 3502–3509. https://doi.org/10.1002/slct.201600812.

(116) Chao, Y. C.; Yeh, S. De; Zan, H. W.; Chang, G. F.; Meng, H. F.; Hung, C. H.; Meng, T. C.; Hsu, C. S.; Horng, S. F. Real-Time and Indicator-Free Detection of Aqueous Nitric Oxide with Hydrogel Film. Appl. Phys. Lett. 2010, 96 (22), 94–97. https://doi.org/10.1063/1.3425895.

(117) Tou, Z. Q.; Koh, T. W.; Chan, C. C. Poly(Vinyl Alcohol) Hydrogel Based Fiber Interferometer Sensor for Heavy Metal Cations. Sensors Actuators B Chem. 2014, 202, 185–

193. https://doi.org/10.1016/j.snb.2014.05.006.

(118) Zheng, J. Hydrogels for Removal of Heavy Metals from Aqueous Solution. J. Environ. Anal. Toxicol. 2012, 02 (07). https://doi.org/10.4172/2161-0525.S2-001.

(119) Barakat, M. A. New Trends in Removing Heavy Metals from Industrial Wastewater. Arab. J. Chem. 2011, 4 (4), 361–377. https://doi.org/10.1016/j.arabjc.2010.07.019.

(120) Chandrangsu, P.; Rensing, C.; Helmann, J. D. Metal Homeostasis and Resistance in Bacteria. Nat. Rev. Microbiol. 2017, 15 (6), 338–350. https://doi.org/10.1038/nrmicro.2017.15.

(121) Ye, B. F.; Zhao, Y. J.; Cheng, Y.; Li, T. T.; Xie, Z. Y.; Zhao, X. W.; Gu, Z. Z. Colorimetric Photonic Hydrogel Aptasensor for the Screening of Heavy Metal Ions. Nanoscale 2012, 4 (19), 5998–6003. https://doi.org/10.1039/c2nr31601c.

(122) Ahmad, JU.; Goni, MA.; Heavy metal contamination in water, soil, and vegetables of the industrial areas in Dhaka, Bangladesh. Environ Monit Assess. 2010, 166, 347–357. https://doi.org/10.1007/ s10661-009-1006-6

(123) Lone, S.; Yoon, D. H.; Lee, H.; Cheong, I. W. Gelatin-chitosan hydrogel particles for efcient removal of Hg(ii) from wastewater. Environ Sci Water Res Technol. 2019, 5, 83–90. https://doi.org/10.1039/ c8ew00678d

(124) Awual, M. R. A novel facial composite adsorbent for enhanced copper (II) detection and removal from wastewater. Chem Eng J. 2014, 266, 368–375. https://doi.org/10.1016/j.cej.2014.12.094

(125) Gupta, A.; Rai, D. K.; Pandey, R. S.; Sharma, B. Analysis of some heavy metals in the riverine water, sediments and fish from river Ganges at Allahabad. Environ Monit Assess. 2009, 157 449–458. https:// doi.org/10.1007/s10661-008-0547-4

(126) Xia, S.; Shen, J.; Wang, J.; Wang, H.; Fang, M.; Zhou, H.; Tanasova, M. Ratiometric Fluorescent and Colorimetric BODIPY-Based Sensor for Zinc Ions in Solution and Living Cells. Sensors Actuators, B Chem. 2018, 258, 1279–1286. https://doi.org/10.1016/j.snb.2017.11.129.

(127) Dai, Y.; Yao, K.; Fu, J.; Xue, K.; Yang, L.; Xu, K. A Novel 2-(Hydroxymethyl)Quinolin-8-Ol-Based Selective and Sensitive Fluorescence Probe for Cd2+ Ion in Water and Living Cells. Sensors Actuators, B Chem. 2017, 251, 877–884. https://doi.org/10.1016/j.snb.2017.05.103.

(128) Vinod Kumar, V.; Anthony, S. P. Silver Nanoparticles Based Selective Colorimetric Sensor for Cd 2+, Hg2+ and Pb2+ Ions: Tuning Sensitivity and Selectivity Using Co-Stabilizing Agents. Sensors Actuators, B Chem. 2014, 191, 31–36. https://doi.org/10.1016/j.snb.2013.09.089.

(129) Hong, M.; Lu, X.; Chen, Y.; Xu, D. A Novel Rhodamine-Based Colorimetric and Fluorescent Sensor for Hg2+ in Water Matrix and Living Cell. Sensors Actuators, B Chem. 2016, 232, 28–36. https://doi.org/10.1016/j.snb.2016.03.125.

(130) Kao, T.-L.; Wang, C.-C.; Pan, Y.-T.; Shiao, Y.-J.; Yen, J.-Y.; Shu, C.-M.; Lee, G.-H.; Peng, S.-M.; Chung, W.-S. Upper Rim Allyl- and Arylazo-Coupled Calix[4]Arenes as Highly Sensitive Chromogenic Sensors for Hg $^{2+}$ Ion. J. Org. Chem. 2005, 70 (8), 2912–2920. https://doi.org/10.1021/jo047880a.

(131) Mizuno, T.; Wei, W.-H.; Eller, L. R.; Sessler, J. L. Phenanthroline Complexes Bearing Fused Dipyrrolylquinoxaline Anion Recognition Sites: Efficient Fluoride Anion Receptors. J. Am. Chem. Soc. 2002, 124 (7), 1134–1135. https://doi.org/10.1021/ja017298t.

(132) Brümmer, O.; La Clair, J. J.; Janda, K. D. A Colorimetric Ligand for Mercuric Ion. Org. Lett. 1999, 1 (3), 415–418. https://doi.org/10.1021/ol990730f.

(133) Taki, M.; Wolford, J. L.; O'Halloran, T. V. Emission Ratiometric Imaging of Intracellular Zinc: Design of a Benzoxazole Fluorescent Sensor and Its Application in Two-Photon Microscopy. J. Am. Chem. Soc. 2004, 126 (3), 712–713. https://doi.org/10.1021/ja039073j.

(134) Chang, G.-F.; Kumar, A.; Ching, W.-M.; Chu, H.-W.; Hung, C.-H. Tetramethyl- m -Benziporphodimethene and Isomeric α,β-Unsaturated γ-Lactam Embedded N-Confused Tetramethyl- m -Benziporphodimethenes. Chem. - An Asian J. 2009, 4 (1), 164–173. https://doi.org/10.1002/asia.200800279.

(135) Song, H.; Liu, G.; Fan, C.; Pu, S. A Novel Fluorescent Sensor for Al3+ and Zn2+ Based on a New Europium Complex with a 1,10-Phenanthroline Ligand. J. Rare Earths 2020. https://doi.org/10.1016/j.jre.2020.02.020.

(136) Lv, J.; Liu, G.; Fan, C.; Pu, S. A Highly Sensitive Fluorescent Sensor for Cd2+ and Zn2+ Based on Diarylethene with a Pyrene Unit. Spectrochim. Acta - Part A Mol. Biomol. Spectrosc. 2020, 227, 117581. https://doi.org/10.1016/j.saa.2019.117581.

(137) Feng, E.; Tu, Y.; Fan, C.; Liu, G.; Pu, S. A Highly Selective and Sensitive Fluorescent Chemosensor for Zn2+ Based on a Diarylethene Derivative. RSC Adv. 2017, 7 (79), 50188–50194. https://doi.org/10.1039/c7ra09966e.

(138) Dong, W. K.; Li, X. L.; Wang, L.; Zhang, Y.; Ding, Y. J. A New Application of Salamo-Type Bisoximes: As a Relay-Sensor for Zn2+/Cu2+ and Its Novel Complexes for Successive Sensing of H+/OH-. Sensors Actuators, B Chem. 2016, 229, 370–378. https://doi.org/10.1016/j.snb.2016.01.139.

(139) Fu, Y.; Tu, Y.; Fan, C.; Zheng, C.; Liu, G.; Pu, S. A Highly Sensitive Fluorescent Sensor for Al3+ and Zn2+ Based on a Diarylethene Salicylhydrazide Schiff Base Derivative and Its Bioimaging in Live Cells. New J. Chem. 2016, 40 (10), 8579–8586.

https://doi.org/10.1039/c6nj01458e.

(140) Lin, Q.; Lu, T. T.; Zhu, X.; Wei, T. B.; Li, H.; Zhang, Y. M. Rationally Introduce Multi-Competitive Binding Interactions in Supramolecular Gels: A Simple and Efficient Approach to Develop Multi-Analyte Sensor Array. Chem. Sci. 2016, 7 (8), 5341–5346. https://doi.org/10.1039/c6sc00955g.

(141) Liu, F.; Fan, C.; Pu, S. A New “Turn-on” Fluorescent Chemosensor for Zn2+ Based on a Diarylethene Derivative and Its Practical Applications. J. Photochem. Photobiol. A Chem. 2019, 371 (November 2018), 248–254. https://doi.org/10.1016/j.jphotochem.2018.11.020.

(142) Waheed, A.; Ahmad, T.; Haroon, M.; Ullah, N. A Highly Sensitive and Selective Fluorescent Sensor for Zinc (II) Ions Based on a 1,2,3-Triazolyl-Functionalized 2,2’-Dipicolylamine (DPA). ChemistrySelect, 2020, 5, 5300 –5305.

(143) Ahmad,T.; Waheed, A.; Abdel-Azeim, S.; Khan,S.; Ullah,N.; Three new turn-on fluorescent sensors for the selective detection of Zn2+: Synthesis, properties and DFT studies, Arabian Journal of Chemistry, 2022, 15(8) 104002, https://doi.org/10.1016/j.arabjc.2022.104002.

(144) Xu, Z.; Yoon, J.; Spring, D.R. Fluorescent chemosensors for Zn2+. Chem. Soc. Rev. 2010, 39, 1996–2006. https://doi.org/10.1039/ b916287a.

(145) Ma, T.H.; Dong, M.; Dong, Y.M.; Wang, Y.W. Peng, Y. A unique water-tuning dual-channel fluorescence-enhanced sensor for aluminum ions based on a hybrid ligand from a 1,10 -binaphthyl scaffold and an amino acid. Chem. - A Eur. J. 2010, 16, 10313–10318. https://doi.org/10.1002/chem.201001431.

(146) Ding, Y.; Tang, Y.; Zhu, W.; Xie, Y.; Fluorescent and colorimetric ion probes based on conjugated oligopyrroles. Chem. Soc. Rev. 2015, 44(5) 1101-1112.

http://dx.doi.org/10.1039/C4CS00436A

(147) Zhang, X.; Katherine S. L.; Alan J.; Stephen J. L.; Water-soluble porphyrins as a dual-function molecular imaging platform for MRI and fluorescence zinc sensing Proceedings of the National Academy of Sciences. 2007, 104(26), 10780-10785. https://www.pnas.org/doi/abs/10.1073/pnas.0702393104}

(148) Lv, Y.; Cao, M.; Li, J.; Wang, J. A Sensitive Ratiometric Fluorescent Sensor for Zinc(II) with High Selectivity. Sensors. 2013, 13, 3131–3141.

(149) Weng, Y. Q.; Yue, F.; Zhong, Y. R.; Ye, B. H. A Copper (II) Ion-Selective On−Off-Type Fluoroionophore Based on Zinc Porphyrin−Dipyridylamino Inorganic Chemistry 2007 46 (19), 7749-7755 DOI: 10.1021/ic061709v.

(150) Weng, Y. Q.; Teng, Y. L.; Yue, F.; Zhong Y. R.; Ye, B. H.; A new selective fluorescent chemosensor for Cu (II) ion based on zinc porphyrin-dipyridylamino. Inorg. Chem. Commun., 2007, 10, 443–446. https://doi.org/10.1016/j.inoche.2006.12.023

(151) Hung, C. H.; Chang, G. F.; Kumar, A.; Lin, G. F.; Luo, L. Y.; Ching, W. M.; Guang Diau, E. Wei. m-Benziporphodimethene: a new porphyrin analogue fluorescence zinc(II) sensor Chem. Commun., 2008, 978–980.

(152) Xu, Z.; Yoon, J.; Spring, D. R. Fluorescent Chemosensors for Zn2+. Chem. Soc. Rev. 2010, 39 (6), 1996–2006. https://doi.org/10.1039/b916287a.

(153) Du, P.; Lippard, S. J. A Highly Selective Turn-on Colorimetric, Red Fluorescent Sensor for Detecting Mobile Zinc in Living Cells. Inorg. Chem. 2010, 49 (23), 10753–10755. https://doi.org/10.1021/ic101569a.

(154) Roy, B.; Bairi, P.; Nandi, A. K. Selective Colorimetric Sensing of Mercury(Ii) Using Turn off-Turn on Mechanism from Riboflavin Stabilized Silver Nanoparticles in Aqueous

Medium. Analyst 2011, 136 (18), 3605–3607. https://doi.org/10.1039/c1an15459a.

(155) Liu, H.; Li, S.; Feng, L.; Hua, Y.; Cai, Y.; Yin, M.; Wan, Y.; Wang, H. A Selective Colorimetric and Efficient Removal Strategy for Mercury (II) Using Mesoporous Silver-Melamine Nanocomposites Synthesized by Controlled Supramolecular Self-Assembly. J. Hazard. Mater. 2020, 388 (May), 121798. https://doi.org/10.1016/j.jhazmat.2019.121798.

(156) Abbas, K.; Znad, H.; Awual, M. R. A Ligand Anchored Conjugate Adsorbent for Effective Mercury(II) Detection and Removal from Aqueous Media. Chem. Eng. J. 2018, 334 (October 2017), 432–443. https://doi.org/10.1016/j.cej.2017.10.054.

(157) Li, M.; Lu, H. Y.; Liu, R. L.; Chen, J. D.; Chen, C. F. Turn-on Fluorescent Sensor for Selective Detection of Zn 2+, Cd 2+, and Hg 2+ in Water. J. Org. Chem. 2012, 77 (7), 3670–3673. https://doi.org/10.1021/jo3002744.

(158) Li, M.; Lu,H.Y.; Liu,R.L; Chen,J.D; Chen.C.F.; Turn-On Fluorescent Sensor for Selective Detection of Zn^{2+}, Cd^{2+}, and Hg^{2+} in Water The Journal of Organic Chemistry. 2012 77 (7), 3670-3673 DOI: 10.1021/jo3002744.

(159) Xu, Z. C.; Yoon, J. Y.; Spring, D. R. Fluorescent chemosensors for Zn^{2+} . Chem. Soc. Rev. 2010, 39, 1996−2006. https://doi.org/10.1039/B916287A

(160) Cockrell, G. M.; Zhang, G.; VanDerveer, D. G.; Thummel, R. P.; Hancock, R. D. Enhanced Metal Ion Selectivity of 2,9-Di-(pyrid-2-yl)-1,10-phenanthroline and Its Use as a Fluorescent Sensor for Cadmium (II) J. Am. Chem. Soc. 2008, 130, 1420−1430.

(161) Chen, Y.; Sun, Z. H.; Song, B. E.; Liu, Y. Synthesis of electron deficient acene derivatives via a bidirectional iterative elongation reaction. Org. Biomol. Chem. 2011, 9, 5530−5534.

(162) Cheng, T. Y.; Wang, T.; Zhu, W. P.; Yang, Y. Y.; Zeng, B. B.; Xu, Y. F.; Qian, X. H. Intrinsically fluorescent carbon dots with tunable emission derived from hydrothermal treatment of glucose in the presence of monopotassium phosphate. Chem. Commun. 2011, 47, 3915−3917.

(163) Komatsu, K.; Urano, Y.; Kojima, H.; Nagano, T. Development of an Iminocoumarin-Based Zinc Sensor Suitable for Ratiometric Fluorescence Imaging of Neuronal Zinc. J. Am. Chem. Soc. 2007, 129, 13447−13454.

(164) Adhikary, J.; Chakraborty, P.; Samanta, S.; Zangrando, E.; Ghosh, S.; Das,D. Thiocyanate mediated structural diversity in phenol based "end-off" compartmental ligand complexes of group 12 metal ions: Studies on their photophysical properties and phosphatase like activity, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2017, 178, 114-124, https://doi.org/10.1016/j.saa.2017.01.041.

(165) Natale, D.; Mareque-Rivas, J.C.; The combination of transition metal ions and hydrogen-bonding interactions. Chem. Commun. 2008, 425.

(166) Jiang,P.; Guo,Z; Fluorescent detection of zinc in biological systems: recent development on the design of chemosensors and biosensors. Coord. Chem. Rev. 2004, 248,205-229

(167) Hu, J.H.; Li, J.B.; Qi, J.; Chen, J.J.; Highly selective and effective mercury (II) fluorescent sensors New J. Chem., 2015,39, 843-848.

(168) Pearson, R. G. Hard and Soft Acids and Bases J. Am. Chem. Soc. 1963, 85, 22, 3533–3539.

(169) Meena, A. K.; Mishra, G. K.; Rai, P. K.; Rajagopal, C.; Nagar, P. N. Removal of Heavy Metal Ions from Aqueous Solutions Using Carbon Aerogel as an Adsorbent. J. Hazard. Mater. 2005, 122 (1–2), 161–170. https://doi.org/10.1016/j.jhazmat.2005.03.024.

(170) Namasivayam, C.; Ranganathan, K. Removal of Pb(Ii), Cd(Ii), Ni(Ii) and Mixture of Metal Ions by Adsorption onto 'waste' Fe(Iii)/Cr(Iu) Hydroxide and Fixed Bed Studies.

Environ. Technol. (United Kingdom) 1995, 16 (9), 851–860. https://doi.org/10.1080/09593330.1995.9618282.

(171) Wang, X.; Deng, W.; Xie, Y.; Wang, C. Selective Removal of Mercury Ions Using a Chitosan-Poly(Vinyl Alcohol) Hydrogel Adsorbent with Three-Dimensional Network Structure. Chem. Eng. J. 2013, 228, 232–242. https://doi.org/10.1016/j.cej.2013.04.104.

(172) Karbarz, M.; Khalil, A. M.; Wolowicz, K.; Kaniewska, K.; Romanski, J.; Stojek, Z. Efficient Removal of Cadmium and Lead Ions from Water by Hydrogels Modified with Cystine. J. Environ. Chem. Eng. 2018, 6 (4), 3962–3970. https://doi.org/10.1016/j.jece.2018.05.054.

(173) Lone, S.; Yoon, D. H.; Lee, H.; Cheong, I. W. Gelatin-Chitosan Hydrogel Particles for Efficient Removal of Hg(Ii) from Wastewater. Environ. Sci. Water Res. Technol. 2019, 5 (1), 83–90. https://doi.org/10.1039/c8ew00678d.

(174) Ozay, H.; Ozay, O. Rhodamine Based Reusable and Colorimetric Naked-Eye Hydrogel Sensors for Fe3+ Ion. Chem. Eng. J. 2013, 232, 364–371. https://doi.org/10.1016/j.cej.2013.07.111.

(175) Joseph, K. A.; Dave, N.; Liu, J. Electrostatically Directed Visual Fluorescence Response of DNA-Functionalized Monolithic Hydrogels for Highly Sensitive Hg2+ Detection. ACS Appl. Mater. Interfaces 2011, 3 (3), 733–739. https://doi.org/10.1021/am101068c.

(176) Sahu, S.; Bishoyi, N.; Patel, R.K. Cerium phosphate polypyrrole fower like nanocomposite: a recyclable adsorbent for removal of Cr (VI) by adsorption combined with in-situ chemical reduction. J Ind Eng Chem. 2021, 99, 55–67. https://doi.org/10.1016/j.jiec.2021.03.041

(177) Sahu, S.; Sahu, U.K.; Patel, R.K.; Modifed thorium oxide polyaniline core-shell

nanocomposite and its application for the efcient removal of Cr (VI). J Chem Eng Data. 2019, 64 (3), 1294–1304. https:// doi.org/10.1021/acs.jced.8b01225

(178) Sahu, S.; Mallik, L.; Patel, R.K. et al Facile synthesis of poly o-toluidine modifed lanthanum phosphate nanocomposite as a superior adsorbent for selective fuoride removal: a mechanistic and kinetic study. Chemosphere. 2020, 252, 126551. https://doi.org/10.1016/j.chemo sphere.2020.126551

(179) Dave, N.; Chan, M. Y.; Huang, P. J. J.; Smith, B. D.; Liu, J. Regenerable DNA-Functionalized Hydrogels for Ultrasensitive, Instrument-Free Mercury(II) Detection and Removal in Water. J. Am. Chem. Soc. 2010, 132 (36), 12668–12673. https://doi.org/10.1021/ja106098j.

(180) Awual, M. R. Novel Nanocomposite Materials for Efficient and Selective Mercury Ions Capturing from Wastewater. Chem. Eng. J. 2017, 307, 456–465. https://doi.org/10.1016/j.cej.2016.08.108.

(181) Ding, Y.; Zhu, W.; Xu, Y.; Qian, X. A Small Molecular Fluorescent Sensor Functionalized Silica Microsphere for Detection and Removal of Mercury, Cadmium, and Lead Ions in Aqueous Solutions. Sensors Actuators, B Chem. 2015, 220, 762–771. https://doi.org/10.1016/j.snb.2015.05.113.

(182) Gupta, V. K.; Sharma, S. Removal of Cadmium and Zinc from Aqueous Solutions Using Red Mud. Environ. Sci. Technol. 2002, 36 (16), 3612–3617. https://doi.org/10.1021/es020010v.

(183) Kadirvelu, K.; Goel, J.; Rajagopal, C. Sorption of Lead, Mercury and Cadmium Ions in Multi-Component System Using Carbon Aerogel as Adsorbent. J. Hazard. Mater. 2008, 153 (1–2), 502–507. https://doi.org/10.1016/j.jhazmat.2007.08.082.

(184) Rocha, C. G.; Zaia, D. A. M.; Alfaya, R. V. da S.; Alfaya, A. A. da S. Use of Rice Straw as Biosorbent for Removal of Cu(II), Zn(II), Cd(II) and Hg(II) Ions in Industrial Effluents. J. Hazard. Mater. 2009, 166 (1), 383–388. https://doi.org/10.1016/j.jhazmat.2008.11.074.

(185) Perumal, S.; Atchudan, R.; Yoon, D. H.; Joo, J.; Cheong, I. W. Spherical chitosan/gelatin hydrogel particles for removal of multiple heavy metal ions from wastewater. Ind Eng Chem Res 2019, 58, 9900–9907. https://doi.org/10.1021/acs.iecr.9b01298

(186) Perumal, S.; Atchudan, R.; Yoon, D.H.; Joo, J.; Cheong, I.W. Graphene oxide-embedded chitosan/gelatin hydrogel particles for the adsorptions of multiple heavy metal ions. J Mater Sci.2020, 55, 9354– 9363. https://doi.org/10.1007/s10853-020-04651-1

(187) Milosavljevic, N.; Debeljkovic, A.; Krušic, M.K.; Milašinovic, N.; Üzüm, Ö.B.; Karadag, E. Application of poly (acrlymide-co-sodium methacrylate) hydrogels in copper and cadmium removal from aqueous solution. Environ Prog Sustain Energy. 2014, 33, 824–834. https://doi.org/10.1002/ep.11854

(188) Sharaf, M.A.; Arida, H.A.; Sayed, S.A.; Younis, A.A.; Farag, A.B. Separation and preconcentration of some heavy-metal ions using new chelating polymeric hydrogels. J Appl Polym Sci. 2009, 113, 1335–1344. https://doi.org/10.1002/app.30137

(189) Lv, Q.; Hu. X.; Zhang, X.; Huang, L.; Liu, Z.; Sun, G. Highly efcient removal of trace metal ions by using poly (acrylic acid) hydrogel adsorbent. Mater Des, 2019, 181, 107934. https://doi.org/10.1016/j. matdes.2019.107934

(190) Atta, A.; Ismail, H.S.; Mohamed, H.M.; Mohamed, Z.M. Acrylonitrile/ acrylamidoxime/2-acrylamido-2-methylpropane sulfonic acidbased hydrogels: synthesis, characterization and their application in the removal of heavy metals. J Appl Polym Sci. 2011, 122, 999–1011. https://doi.org/10.1002/app.34245

(191) Kong, C.; Zhao, X.; Li, Y.; Yang. S.; Chen, Y.M.; Yang, Z.; Ioninduced synthesis of alginate fbroid hydrogel for heavy metal ions removal. Front Chem. 2020, 7, 905. https://doi.org/10.3389/fchem. 2019.00905

(192) Bai, C.; Wang, L.; Zhu, Z.; Adsorption of Cr (III) and Pb (II) by graphene oxide/alginate hydrogel membrane: characterization, adsorption kinetics, isotherm and thermodynamics studies. Int J Biol Macromol. 2020, 147, 898–910. https://doi.org/10.1016/j.ijbiomac. 2019.09.249

Chapter 2

Scope of the work and Objectives

2.1 Scope of the work

Mostly developed sensors suffer from poor sensing properties including sensitivity and selectivity, high light scattering, low binding affinities. A large number of fluorescent probes (e.g., Fluorescein[1], dansyl[2], anthracene[3].) have been synthesized and utilized in sensing and biological imaging but almost all shows high background fluorescence and low increase in fluorescence intensity.[4] Colorimetric sensors for heavy metal ions based on hydrogel in an aqueous medium with satisfactory comprehensive performance are scarce. Visual detection is an increasingly attractive method in various fields because both qualitative and semi-qualitative analyses can be performed without any advanced or complicated instrumentation. Current techniques require costly and sophisticated equipment for heavy metal ion detection, e.g., ICPAES and AAS. Since most of the toxic metals are found in waste water. The detection of heavy metals in aqueous systems has become very important and challenging due to the common co-existence of other metal ions. Therefore, there is a need of development of sensors which can sense metal ions in water.[5]

Zinc, cadmium and mercury are spectroscopically silent metals therefore techniques such as electron paramagnetic resonance and nuclear magnetic resonance spectroscopy cannot be used for their detection. No colorimetric sensor is available to sense Zn^{2+}, Cd^{2+} and Hg^{2+} in environment and biological samples based on color changing molecule embedded polymeric hydrogels.[6] Colorimetric sensors for heavy metal ions based on hydrogel in an aqueous medium with satisfactory comprehensive performance are scarce. For instance, a novel hydrophilic colorimetric sensor which could easily detect spectroscopically silent zinc, cadmium and mercury ions in water and in bacterial or human cells. To have better sensitivity, most colorimetric sensors are diffused in sample solution for full interaction with the target substance, but sometimes the uneven and unstable dispersion of the sensors induces unsteady detection results. To avoid this problem, chemo sensor can be assembled on a solid substrate and the selection of a solid substrate is most important as it can considerably affect the sensitivity of the sensor. Hydrogels are perfect for optical sensor immobilization owing good biocompatibility, better sensor loading capacity, and very low optical background. Further, by mixing with different monomers hydrogel backbone property such as charge and hydrophobicity can be modified, allowing control of sensor performance. They are the better candidate for metal ions sensor formulations. The development of easy, inexpensive, and reliable analytical tools for real-time on-site detection of toxic metal ions in various biological and environmental samples is still in great demand.[7]

Several techniques have been developed to eliminate heavy metal ions from wastewater but each one exhibits limitations for instance in case of solvent extraction the eluent has to be processed to avoid any further pollution. Chemical precipitation of toxic sediments is not an economically successful method, then regarding adsorption of pollutants on solid sorbents appeared to be an efficient technique. Among all this adsorption technique is widely regarded as an easy, effective and versatile method for the removal of heavy metals from aqueous solution. The potential of hydrogels to be complex with metal ions allows them to be an efficient metal absorbent. Although hydrogels are found to be superior candidate for the removal of a wide range of aqueous pollutants, including heavy metals, dyes and other emerging contaminates but selective adsorption of contaminates is rarely explored. Therefore, research efforts are required to develop hydrogels with the desired properties, sensitivity and selectivity toward a specific pollutant. Removal of heavy metal ions from aqueous medium using different formulations of hydrogel based on biopolymers such as raw wool, carboxymethyl tamarind, carboxymethyl guar gum to be further explored.[7,8]

2.2 Objectives

- To develop a robust procedure for the visual on-site detection of spectroscopically silent metals zinc, cadmium and mercury in an aqueous medium using a color changing molecule embedded polymeric hydrogel matrix-based colorimetric sensor.
- To develop a sensor which provides on-site visual naked eye detection of spectroscopically silent Zn^{2+}, Cd^{2+} and Hg^{2+} metal ions in real industrial wastewater and of Zn^{2+} in animal and bacterial cells.
- To developed a robust and cost-effective adsorbent for removal of Zn^{2+}, Cd^{2+} and Hg^{2+} from aqueous solution.

2.3 References

(1) Corradini, R.; Dossena, A.; et al. Chiral Recognition and Separation of Amino Acids by Means of a Copper (II) Complex of Histamine Monofunctionalized beta.-Cyclodextrin. Journal of the American Chemical Society. 1994, 116 (22), 10267-10274. DOI: 10.1021/ja00101a050.

(2) Torrado, A.; Walkup,G.K.; Imperiali, B.; Exploiting Polypeptide Motifs for the Design of Selective Cu(II) Ion Chemosensors. Journal of the American Chemical Society. 1998, *120* (3), 609-610. DOI: 10.1021/ja973357k.

(3) Chang, C.J.; Jaworski, J.; Nolan, E.M.; Sheng, M.; Lippard, S.J. A tautomeric zinc sensor for ratiometric fluorescence imaging: Application to nitric oxide-induced release of intracellular zinc. Proceedings of the National Academy of Sciences. 2004, 101(5), 1129-1134. https://www.pnas.org/doi/pdf/10.1073/pnas.0308079100

(4) Kumar, R.; Kumar, A. et al. meta -Benziporphodimethenes: New Cell-Imaging Porphyrin Analogue Molecules. 2016, 1(3), 3502-3509. https://doi.org/10.1002/slct.201600812.

(5) Ye B.F.; Zhao Y.J.; Cheng Y.; et al. Colorimetric photonic hydrogel aptasensor for the screening of heavy metal ions. Nanoscale. 2012, 4, 5998–6003. DOI:10.1039/ c2nr31601c.

(6) Li, M.; Lu, H.Y.; Liu, R.L.; Chen, J.D.; Chen, C.F. Turn-On Fluorescent Sensor for Selective Detection of Zn^{2+}, Cd^{2+}, and Hg^{2+} in Water. The Journal of Organic Chemistry. 201, 77 (7), 3670-3673. DOI: 10.1021/jo3002744.

(7) Meena A. K.; Mishra G. K.; Rai, P.K.; Rajagopal, C.; Nagar, P.N. Removal of heavy metal ions from aqueous solutions using carbon aerogel as an adsorbent. J Hazard Mater. 2005, 122, 161–170. https://doi. org/10.1016/j.jhazmat.2005.03.024.

(8) Karbarz, M.; Khalil A.M.; Wolowicz, K.; Kaniewska, K.; Romanski, J.; Stojek, Z.; Efficient removal of cadmium and lead ions from water by hydrogels modified with cystine. J Environ Chem Eng. 2018, 6, 3962–3970. https://doi.org/10.1016/j.jece.2018.05.054.

Chapter 3

Fabrication of a Metal ion Sensor using *Meta*-Benziporphodimethene Embedded Polymeric Hydrogel

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3.1 Introduction

Though, metal ions play vital roles in biology, but even nectar is a poison if taken to excess. Thus, surplus levels of metal ions in living bodies can lead to malfunctioning in respiration, growth, gene transcriptions, enzymatic reactions and immune functions.[1] Heavy metals are extensively present in the air, water, and soil as a result of solid waste incineration, fossil fuel burning, chemical, mining industries and metal smelting.[1-3] The monitoring of Zn^{2+} in living cells and tissue is very crucial owing to its predominant functions as signaling agents to mediate processes such as gene expression, neurotransmission, apoptosis, cell growth and division.[4] Disturbance of zinc homeostasis in human bodies have resulted in health disorders like Alzheimer’s disease, diabetes, and several neurodegenerative disorders.[5] Cadmium is one of the most common toxic metallic pollutants even at very low concentrations. Cadmium has detrimental effects on humans causing brain development disorders, chronic inflammation to the heart and kidney, renal dysfunction, and impairing reproductive systems. Mercury ions have high affinity for thiol groups (-SH) present in proteins and enzymes. Consequently, the presence of Hg^{2+} ions in human bodies leads to the dysfunction of cells in the kidney, brain, and central nervous system. It is highly desirable to monitor Zn^{2+}, Cd^{2+} and Hg^{2+} ions, efficiently and sensitively. Therefore, the need of the hour is to develop a novel probe for the detection of these metal ions in both biological and environmental systems. [6–8]

The colorimetric hydrogel sensor can easily recognize metal ions in aqueous medium by naked eyes and monitored color change with different metal ions concentration without any complicated instrumental analysis. Metallochromic dyes change color on complexing with certain metal ion are introduced to develop colorimetric sensors. To achieve immobilized dyes into hydrogel, they are first modified to acrylic monomer using esterification reaction. Hydrogels functionalized with dyes are prepared in the forms of bulk and porous by using monomer functionalized with dye and worked to manufacture user-friendly sensing kit. For instance, 4-(2-pyridylazo) resorcinol (PAR) have been modified with vinyl moiety to incorporate it into vinyl-based hydrogel. PAR is one of organic chelate to sense specific bivalent metal (such as Co, Ni, Cu, etc.) and was selected to be broadly applicable than other organic chelate that detect only one metal at a time.[9] Two fluorescent probes incorporated in a highly dense manner, in the hyperbranched poly (poly (ethylene glycol) diacrylate) (HB-PEGDA) and thiolated sodium alginate (SA-SH) composite hydrogel microspheres. It was used to construct the sensor, and were prepared by using a self-assembly process in conjunction with a microfluidic device.[10]

In our case the *in-situ* incorporation of 11, 16-bis (phenyl)-6, 6, 21, 21- tetramethyl-m-benzi-6,21-porphodimethene (*meta*-BPDM) ligand was achieved without any pre- modification in a host hydrogel. The synthesis of *meta*-BPDM-embedded PAM/CMG hydrogels was performed using water as a solvent. The main advantage of our synthesized sensor is that *meta*-BPDM ligand does not leach out from the hydrogel matrix after metalation with metal ions in aqueous system or even without metalation during the sensing studies. The hydrophilic nature of polymeric hydrogels enables metal ions in an aqueous environment to diffuse into the polymeric network containing *meta*-BPDM and reacts with it causing color change from red to bluish-green. The detection of heavy metals in aqueous systems has become very important and challenging due to the common co-existence of other metal ions. The synthesized sensor does not show any change in color due to interfering metal ions such as alkali, alkaline and other transition metal ions. The sensor changes color only when bound with Zn^{2+}, Cd^{2+} and Hg^{2+} separately as well as in the mixture of three metal ions which is a clear advantage for on-site inspection. The sensor changes color due to the specific binding of physically engulfed meta-BPDM with these metal ions in the presence of other metal ions.

To the best of our knowledge no colorimetric sensor is available to sense Zn^{2+}, Cd^{2+} and Hg^{2+} in aqueous medium based on color changing molecule embedded polymeric hydrogels. *meta*-BPDM is an organic moiety containing pyrrolic and carbocyclic unit's insoluble in aqueous medium. Therefore, it cannot be used directly as a sensor in water and requires a hydrophilic matrix which can be a mediator between water and *meta*-BPDM. To sense Zn^{2+}, Cd^{2+} and Hg^{2+} metal ions in water effectively is a great challenge for scientists. The hydrophilic nature of polymeric hydrogels enables metal ions in an aqueous environment to diffuse into the polymeric network containing *meta*-BPDM and react with it causing color change from red to bluish green. The porous matrix of the hydrogels allows small molecules and ions to penetrate into the hydrogels through diffusion. Usually, hydrogels have physically well-defined three-dimensional hydrophilic porous structure and chemically active functional group which makes them to capture metal ions from water and form stable complexes. Novel methods that fulfill the criteria of required selectivity, sensitivity, good biocompatibility and lesser background disturbance in natural framework are continuously being explored.[11] The synthesized hydrogel is used as a colorimetric probe for the *on-site* visual selective detection of Zn^{2+}, $Cd^{2+}$and Hg^{2+} in aqueous medium.

3.2 Experimental Section

3.2.1 Materials

Pyrrole and substituted aldehydes (liquid) were distilled prior to use. α,α dihydroxy-1, 3-diisopropylbenzene (TCI) and boron trifluoride ethyl ether complex, 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) were used as supplied (SRL). Solvents and all other reagents were used as such without purification. Silica gel was obtained from Merck. Carboxymethyl guar gum was procured from Hindustan Gum and Chemicals Ltd., Bhiwani, Haryana (India). Potassium persulfate ($K_2S_2O_8$) was obtained from Thomas Baker chemicals, Acetone and N, Ń-methylenebisacrylamide (MBA) were purchased from Merck Germany and Acrylamide from SRL. All reagents were used as obtained. All solutions were prepared in deionized water.

3.2.2. Synthesis

Polyacrylamide/ carboxymethyl guar gum hydrogel: In a 100 mL beaker acrylamide (2.5 g) was dissolved in 25 mL distilled water. $K_2S_2O_8$ (0.025 g), N, Ń- methylenebisacrylamide (0.05 g) and carboxymethylguargum (0.5 g) were added and stirred for 1 hour after that the reaction mixture was transferred into test tubes and placed in water bath at 60℃ up to gel formation. The hydrogel was obtained by breaking the test tubes and then cut into slices, washed with distilled water to remove unreacted chemicals, firstly dried at room temperature and then in the oven to obtain a dried form of hydrogels.[12]

***meta*-Benziporphodimethenes embedded polyacrylamide/carboxymethyl guar gum:** *meta*-BPDM was synthesized as reported elsewhere.[13] *meta*-BPDM embedded PAM/CMG hydrogels were synthesized successfully using a mixture of acrylamide (2.5 g in 20 mL distilled water) and *meta*-BPDM (4 mg in 5 mL acetone:H_2O (1:1) was taken in a beaker. $K_2S_2O_8$ (0.025 g), N, Ń-methylenebisacrylamide (0.05 g) and carboxymethyl guar gum (0.5g) were added into the beaker and stirred for 1 hour after that the reaction mixture was transferred into test tubes and placed in water bath at 60℃ up to gel formation. The hydrogel was obtained by breaking the test tubes and then cut into slices, washed with distilled water to remove unreacted chemicals, firstly dried at room temperature and then in the oven to obtain a dried form of hydrogels. The color of the obtained hydrogel was red.

3.2.3. Characterization

Thermogravimetric analysis (TGA): The thermogravimetric analysis was carried out with a Perkin Elmer TGA 4000. TGA was performed in an atmosphere of N_2 and up to a temperature of 800℃ starting from 31 ° C. The heating rate was constant in all cases at 10℃/minute.

Scanning electron microscopy (SEM): The morphology was observed by JEOLJSM-6610LV after coated with platinum film.

X-ray diffraction (XRD): X-ray diffraction patterns were analyzed using BRUKER AXS diffractometer. The scattered radiation was detected in the 2ϴ range of 2 to 80˚with a step size of 0.02˚.

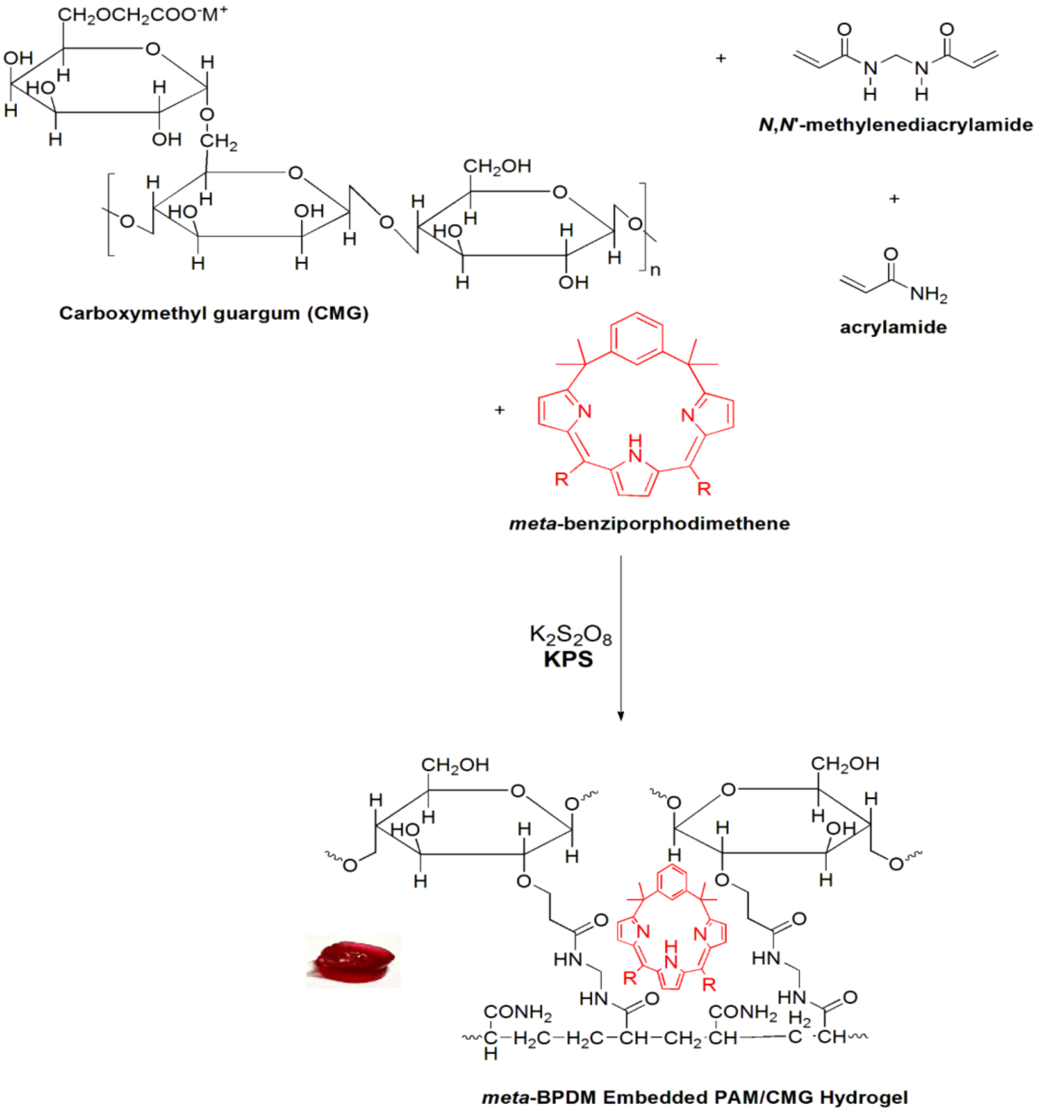
FTIR spectroscopy: The FTIR spectrums were plotted out using NICOLET 380 FTIR Spectrophotometer. Potassium bromide pellet technique was used for FTIR study.

UV-Visible spectroscopy: The UV-visible absorption spectra of synthesized *meta*-BPDM dissolved in dichloromethane was obtained using UV 1800 Shimadzu Spectrophotometer and solid-state UV-visible absorption spectra of *meta*-BPDM embedded hydrogels (powder form) was obtained using PerkinElmer Lambda 750 Spectrometer.

Sensing studies: *meta*-BPDM embedded hydrogels were synthesized and used for the recognition of Zn^{2+}, Cd^{2+} and Hg^{2+}. The *meta*-BPDM embedded hydrogels sensing abilities were scanned in solutions of alkali metal salts, alkaline earth metal salts, $ZnCl_2$, $HgCl_2$, $CdCl_2$ of various concentrations. Time, concentration, temperature dependent sensitivity of *meta*-BPDM embedded hydrogel was noted. Each sensing experiment was performed three times.

3.3 Results and Discussion

3.3.1. Synthesis: The synthesis of *meta*-BPDM embedded PAM/CMG hydrogels was performed using water as solvent. All reactants were soluble in water except *meta*-BPDM. To overcome this difficulty a mixture of acetone and water (1:1) were found to be the best composition for dissolving *meta*-BPDM. The synthesis of *meta*-BPDM was repeated using reported protocols in our earlier reports. The spectral data matches with the reported literature[13]. The synthesis of *meta*-BPDM embedded polymeric hydrogel was achieved *in-situ* formation of hydrogel in the presence of *meta*-BPDM (scheme 3.1). The red color of the *meta*-BPDM is retained in the *meta*-BPDM embedded PAM/CMG hydrogel. The presence of embedded *meta*-BPDM was further confirmed with UV-visible spectroscopy.



Scheme 3.1. Synthesis of *meta*-BPDM embedded PAM/CMG hydrogel.

3.3.2. Thermogravimetric analysis (TGA): Thermogravimetric analysis is a method to assess the thermal stability of various substances by studying their decomposition pattern. TGA is also used to investigate the thermal stability of the polymers. In this technique, the weight loss of the sample is measured with respect to time as a function of temperature. This method also gives data about adsorption, absorption, desorption and thermal decomposition. The instrument used in TGA is known as thermogravimetric analyzer that comprised of a precision balance with a sample holder situated inside the furnace. Usually, the temperature is raised with the constant rate and reaches up to 1000 °C during the thermal reaction under inert atmosphere, especially N_2 gas and weight percentage is measured. In addition, TGA provides a curve between mass percentage and temperature. When the sample material is thermally stable, the mass change will not be observed therefore no slope in the TGA trace.[14-16]

The TGA curve of PAM/CMG hydrogel is similar to *meta*-BPDM embedded PAM/CMG hydrogel which indicates that *meta*-BPDM does not affect thermal behavior of hydrogel which may be attributed that *meta*-BPDM does not involve in any kind of chemical bond formation with the hydrogel but hydrogen bonding interaction may occur. Nevertheless, we cannot rule out any π-π stacking like interaction of *meta*-BPDM itself and other hydrogen bonding interaction with the –NH of *meta*-BPDM with the freely available –OH or –NH group on the hydrogel. *meta*-BPDM-Zn^{2+}-PAM/CMG hydrogel shows different degradation behavior. This may be attributed due to a change in the geometry of *meta*-BPDM once metalated. The early weight loss in hydrogels is due to evaporation of adsorbed water molecules. The main decomposition starts above 200 ℃. The second zone of weight loss is 250℃ to 350 ℃. This is because of the degradation of the carboxymethyl group, hydroxyl group. The third zone of weight loss at 350℃ to 450℃ is due to the degradation of polymer backbone, crosslinking, amide groups and the final weight loss at 450℃ to 600℃ due to the degradation of C-O-C, organic backbone and in case of *meta*-BPDM embedded hydrogels degradation of *meta*-BPDM backbone occurs i.e., the decomposition of macrocyclic ring, benzene, pyrrole moiety (Fig 3.1). We were not interested in quantifying the amount of zinc metal ions or other absorbed through TGA analysis. Here using this TGA technique only thermal stability of hydrogels was observed.

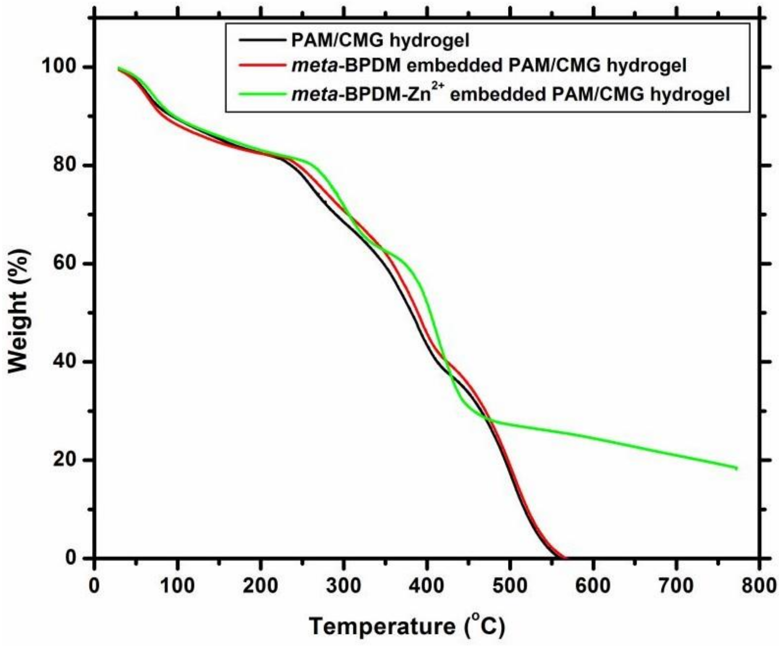


Fig.3.1. TGA curves of PAM/CMG, *meta*-BPDM embedded PAM/CMG and *meta*-BPDM-Zn^{2+}-PAM/CMG hydrogel.

3.3.3. Scanning Electron Microscopy (SEM):

SEM is a strong technique gives information about sample morphology, topography, and crystallographic information. It produces a two-dimensional image of the specimen. For mounting the material, it should be dried, since this technique is based on the electron beam sample should be electrically conducting. Therefore, a very thin gold coating is applied by sputtering on the surface of non-conducting material to make it electrically conducting for imaging. The free electron source is thermionic emission gun and these electrons are converted into a fine beam using the magnetic lens. The image is developed by rastering the accelerated beam striking the sample. Various type of signal is produced such as secondary electrons, auger electrons, back-scattered electrons, and x-ray. Which imparts information about the topography, sensitivity and composition of the surface respectively. Mainly secondary electrons are detected for image generation, which displays the topographic surface of the sample.[17] The morphology of synthesized samples was observed at various magnifications and shown in Fig.3.2.

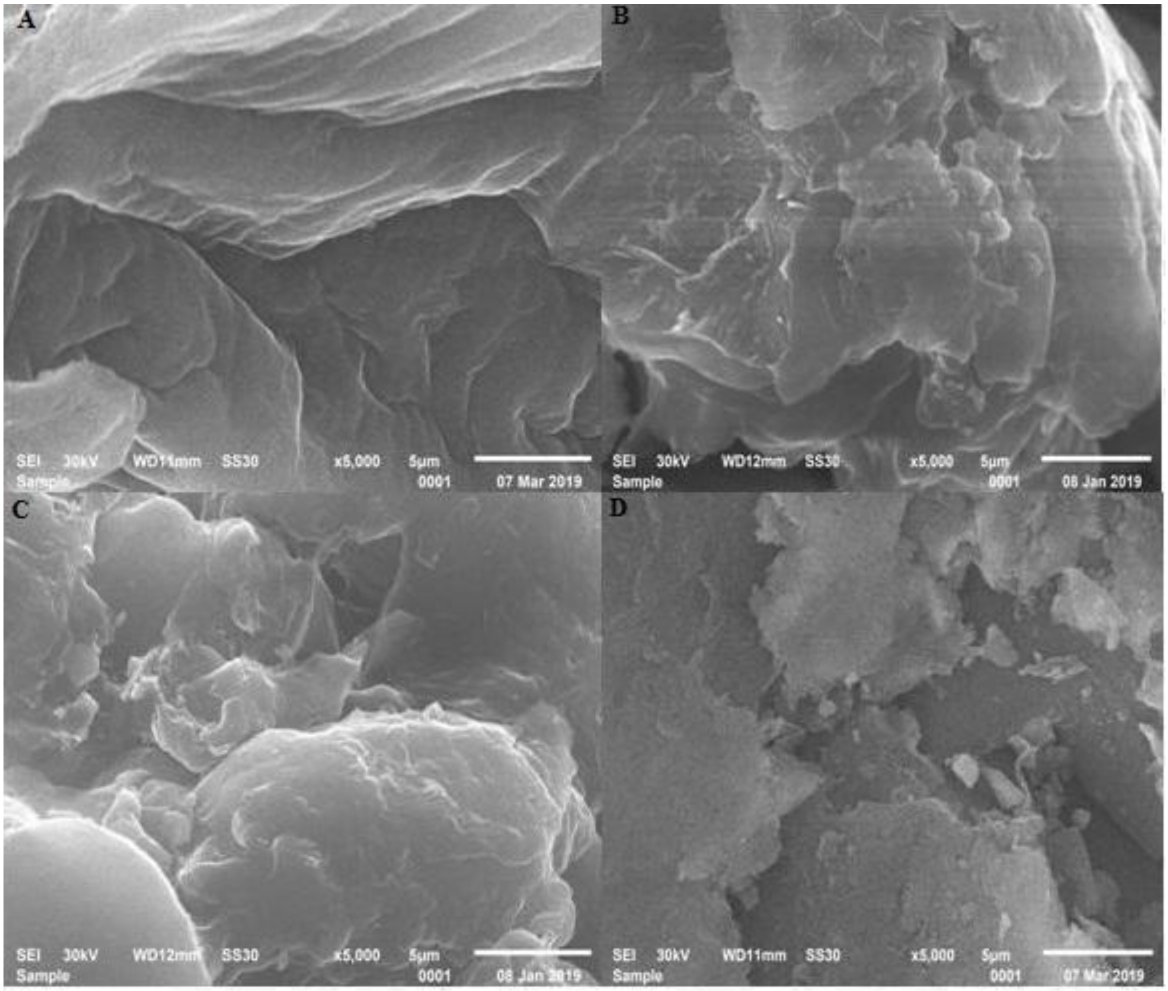


Fig. 3.2. Surface microphotograph of (A) Carboxymethyl Guar Gum (B) PAM/CMG hydrogel (C) PAM/CMG *meta*-BPDM hydrogel (D) PAM/CMG *meta*-BPDM-Zn^{2+} hydrogel.

It is clearly visible from the image of SEM micrograph of Carboxymethyl Guar Gum that it has rough layered and morphology and shown in Fig.3.2 (A) while PAM/CMG hydrogel has spherical layered structure and shown in Fig. 3.2 (B). This change in morphology is due to hydrogel formation and crosslinking between polymeric chains. The uneven and rough surface morphology of *meta*-BPDM embedded PAM/CMG hydrogel and *meta*-BPDM -Zn^{2+} -PAM/CMG hydrogel is unaffected with the insertion of *meta*-BPDM and results are shown in Fig. 3.2 (C) and Fig. 3. 2 (D), respectively. Rough morphology of hydrogel is responsible for metal uptake and enables it to bind with *meta*-BPDM *i.e.*, physically engulfed in hydrogel which does not affect the hydrogel morphology.

3.3.4 X-ray diffraction (XRD):

X-ray diffraction is one of the best techniques for the identification of crystalline or amorphous nature of the materials and various structural properties. It works on the principle of Bragg's law involving a beam of X-ray having the energy (1-100 keV) is incident on the crystal planes of the material and it is scattered by the atoms in all directions. These scattered X-rays can interfere constructively and destructively. In general, XRD provides information about long-range order structure, crystallinity, phase composition, crystal size, shape, micro-stress, and strain. The presence of broad signal is due to the lack of long-range crystallographic order.[18,19]

In Fig. 3.3 PAM/CMG hydrogel XRD spectrum, a broad peak of less intensity was observed which demonstrates that there is no crystalline region hence shows amorphous nature of crosslinked hydrogel. Further decrease in peak intensity was observed in case of *meta*-BPDM embedded PAM/CMG hydrogel. This may be due to the conformation changes upon insertion of *meta*-BPDM in hydrogel. In the case of *meta*-BPDM-Zn^{2+}-embedded PAM/CMG hydrogel slight increase in intensity and crystalline nature was observed and similar with Hg^{2+} and Cd^{2+}. This may be due to the complexation of metal ions with embedded *meta*-BPDM which causes a change in conformation in the polymer backbone. The crystalline region is formed by the H-bonding among

-OH, -NH groups present in the polymeric network. Overall, nothing important regarding metalation and structure of the hydrogel can be interpreted from XRD analysis.

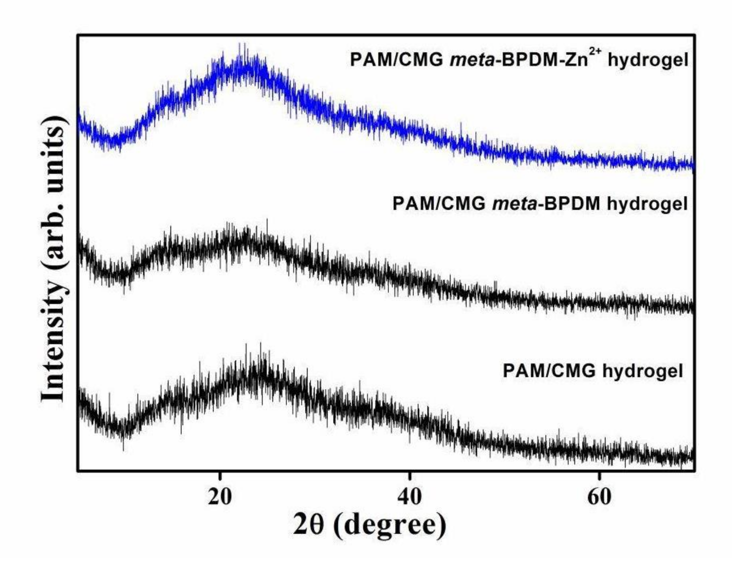


Fig. 3.3. The XRD spectra of hydrogels.

3.3.5. Fourier-Transform Infrared Spectroscopy (FTIR):

The infrared spectroscopy technique used to identify the functional groups in the unknown organic compound. The principle includes the absorption in the infrared region by molecules having bonds involving change in dipole moment while vibration on absorption of infrared radiation and are known as infrared active molecule. The fingerprint region (below 1500 cm^{-1}) contains many characteristics absorption bands due to bending and stretching vibration of the molecules which can be identified easily. Fourier transform is a preferable method to study infrared spectroscopy. Which is connected with a simple optical device called interferometer and generates a signal called interferogram.[20-22] FTIR study was performed to analyze the structure, type of functional groups, nature of bonding interaction between functional groups of all samples before and after hydrogel formation. The FTIR Spectra of all samples are shown in Fig. 3.4.

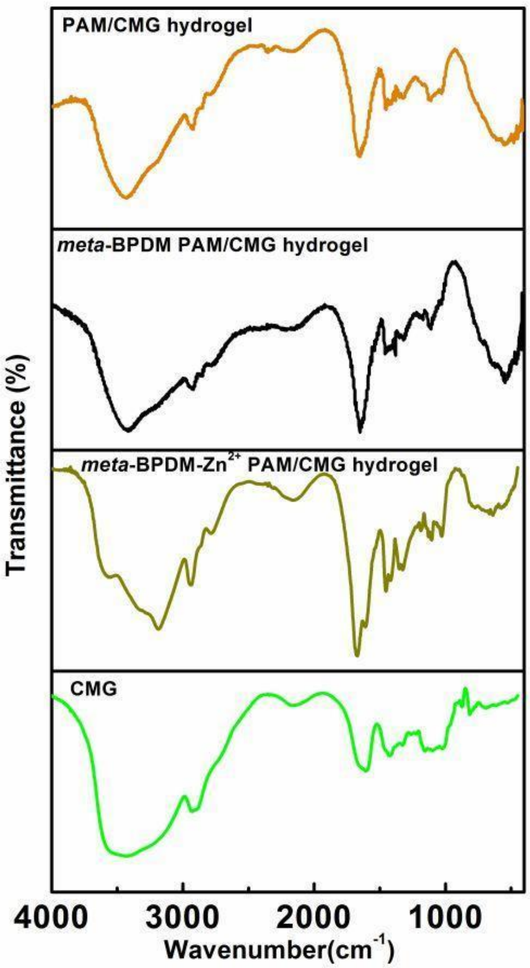


Fig. 3.4 The FTIR spectra of PAM/CMG hydrogel, *meta*-BPDM embedded PAM/CMG hydrogel, PAM/CMG *meta*-BPDM-Zn^{2+} hydrogel and Carboxymethyl guar gum.

Assignment of corresponding peaks are shown in Fig. 3.4. The FTIR spectra of PAM/CMG hydrogel and *meta*-BPDM embedded PAM/CMG hydrogel are almost the same. The stretching and deformation vibrations were observed at 3424 cm^{-1} and 3445 cm^{-1} (O-H stretching), 2914 cm^{-1} and 2936 cm^{-1} (C-H stretching), 1640 cm^{-1} (C=O stretching), 1427 cm^{-1} (C-H and C-N bending). In the FTIR spectra of PAM/CMG *meta*-BPDM-Zn^{2+} hydrogel absorption peak at 3190 cm^{-1} (O-

H stretching), 2936 cm^{-1} (C-H stretching), 1662 cm^{-1} (C=O stretching), 1449 cm^{-1} (C-H and C-N bending). In the FTIR spectra of carboxymethyl guar gum peak at 3467 cm^{-1} (O-H stretching), 2914 cm^{-1}(C-H stretching), 1618 cm^{-1} (C=O stretching), 1427 cm^{-1}(C-H and C-N bending). The difference in absorption and intensity of peaks is due to crosslinking and metalation of polymeric hydrogels. The observed spectra show that insertion of *meta*-BPDM does not affect the absorption pattern but it's metalation affects. This is because metalation of *meta*-BPDM changes its conformational geometry.

3.3.6. Ultraviolet-Visible Spectroscopy: The ultraviolet (UV) region includes approximately the 10–380 nm wavelength range of the electromagnetic spectrum. Since it involves excitation of the outermost electrons of the atoms, which are involved in the formation of molecules therefore, it is also referred to as "electronic spectroscopy". When the frequency of incident radiation corresponds to the energy difference between two energy levels that specific frequency is absorbed by the sample causing electronic transition between them. This energy difference depends on the electronic structure and environment of the molecule. This phenomenon causes distribution of the electronic density in the outermost orbitals of an individual atom and in case of molecular orbitals electronic transition occurs from the occupied molecular orbitals to the unoccupied molecular orbitals. Which decides the absorption bands in the UV-Vis region. For a transition to occur after absorption of incident radiation it is necessary to result in dislocation of charge and follow some rules, such as Spin Multiplicity Selection Rule, Laporte Selection Rule, and Coupling Interaction with adjacent cations, have to be respected.[23,24]

The synthesis of *meta*-BPDM was confirmed by using UV-visible absorption spectra as shown in Fig.3.5 (A) and spectral values match with the reported literature elsewhere.[13] *meta*-BPDM has been reported to sense Zn^{2+}, Cd^{2+} and Hg^{2+} in organic solvent i.e., acetonitrile in our earlier reports.[13,25,26] To ensure the engulfing of *meta*-BPDM in hydrogel, the solid-state UV-visible spectra of *meta*-BPDM embedded in PAM/CMG was recorded at room temperature and shown in Fig. 3. 5(B). The recorded spectra show similar spectra as for free *meta*-BPDM which confirms *meta*-BPDM is physically engulfed in a network of hydrogels.[27-29] The UV-visible absorption spectra of *meta*-BPDM embedded in PAM/CMG hydrogel is broad due to discrete conjugated system, high energy Soret band is observed between 333 nm whereas low energy broad Q bands are observed at 515 nm and 560 nm. The metalation was observed with the change in color from red to bluish green upon addition of dried *meta*-BPDM embedded polymeric hydrogel 60 mg into aqueous solution 50 mg/L of individual M^{2+} (M = Zn, Hg and Cd) separately. Further, it was confirmed by shifting of visible band or low energy Q bands in UV-Visible Spectra from 560 nm to 670 nm. The solid-state UV-vis spectra corresponding to Zn^{2+}, $Cd^{2+}$and Hg^{2+} metalated hydrogel was found to be the same and the observed UV-vis values match with the reported literature.[13,25,26] Since we want to observe only the sensing of Zn^{2+}, Cd^{2+} and Hg^{2+} in water therefore the hydrogel was not allowed in the metal ion solution for longer to get complete metalation. The significant red shift of visible bands as shown in Fig. 3.5(C) is because of metalation.[13,26,30] To verify that *meta*-BPDM does not leach out into the aqueous solution of metal ions the UV-vis spectra of the water was taken before and after adding hydrogel during the sensing experiment. The observed spectra do not show any of the *meta*-BPDM absorption peaks. which confirms that it has not leached out of the hydrogel into water.

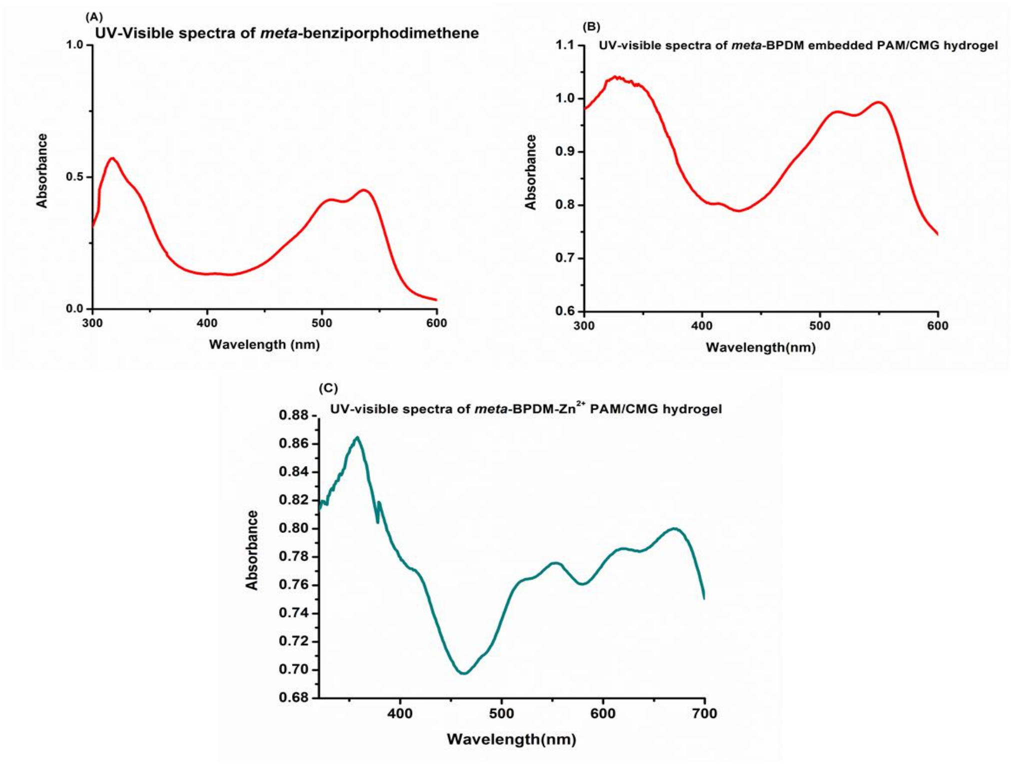
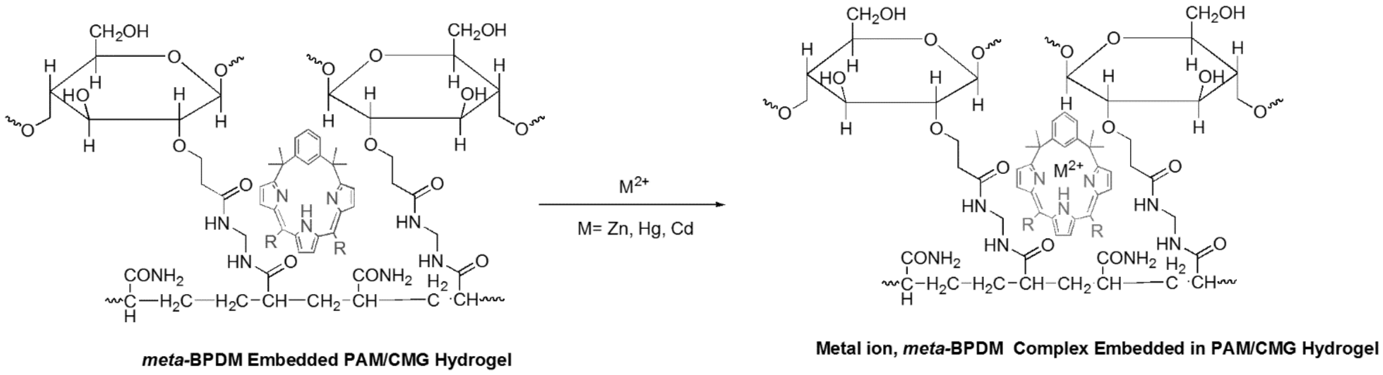


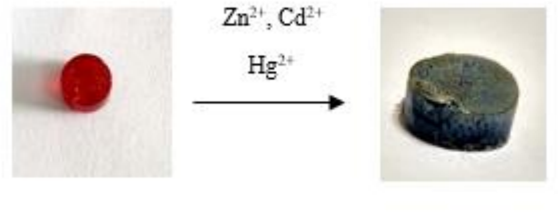
Fig. 3.5 (A) The UV-Visible spectra of synthesized *meta*-BPDM. (B) Solid state UV-Visible spectra of *meta*-BPDM embedded in PAM/CMG hydrogel and (C) Zn^{2+} Metalated *meta*-BPDM in PAM/CMG hydrogel.

3.3.7. Sensing Studies:

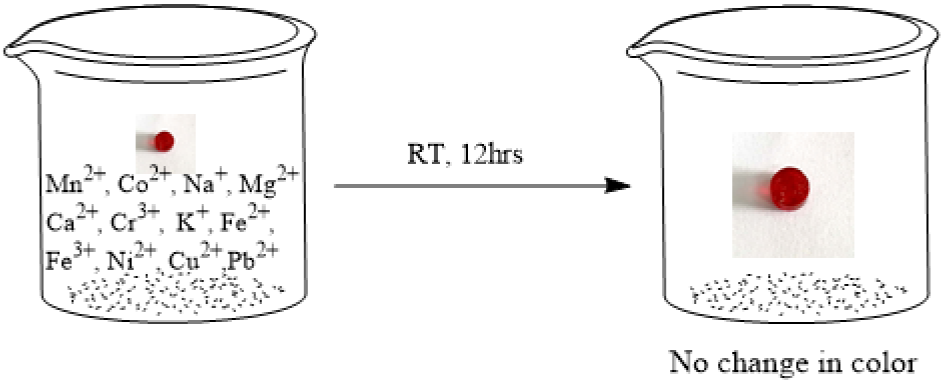
(A)



(B)


Zn2+, Cd2+
Hg2+

(C)


Mn2+, Co2+, Na+, Mg2+
Ca2+, Cr3+, K+, Fe2+,
Fe3+, Ni2+, Cu2+,Pb2+
RT, 12hrs
No change in color

(D)

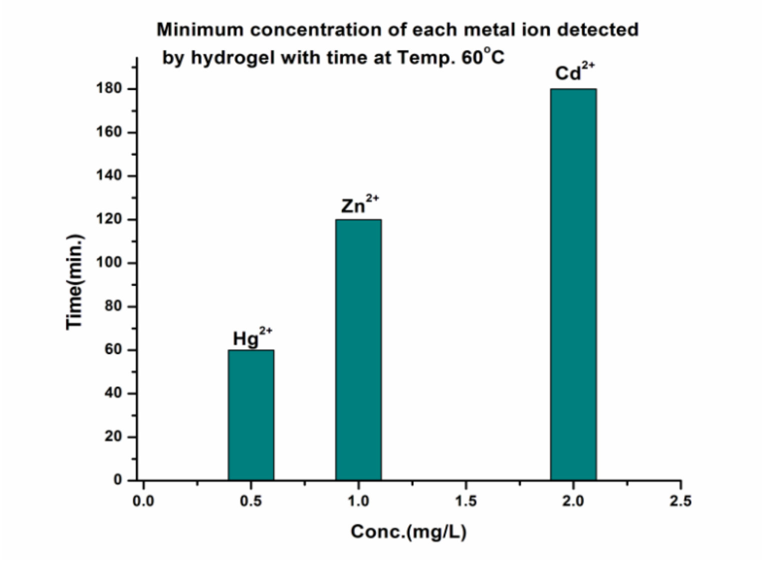

Minimum concentration of each metal ion detected
by hydrogel with time at Temp. 60°C
Time(min.)
Conc.(mg/L)
0
20
40
60
80
100
120
140
160
180
0.0
0.5
1.0
1.5
2.0
2.5
Hg2+
Zn2+
Cd2+

Fig.3.6 Sensing studies using *meta*-BPDM embedded polymeric hydrogels, a change in color was obtained with Zn^{2+}, Cd^{2+} and Hg^{2+} only in presence of other metal ions.

My main focus was to develop a sensor in aqueous medium for Zn^{2+}, Cd^{2+} and Hg^{2+}. Since all the three metal ions are spectroscopically silent therefore their simultaneous detection is very challenging. The *meta*-BPDM molecule is insoluble in water and does not sense metal ions directly in aqueous medium, therefore, it has been used through a hydrogel matrix. which acts as a mediator between water and *meta*-BPDM. The sensing ability of the synthesized polyacrylamide/carboxymethyl guar gum polymeric hydrogel was checked in aqueous medium. *meta*-BPDM is a red colored molecule that has been incorporated *in-situ* in hydrogel synthesis. The *meta*-BPDM changes color upon metalation with Zn^{2+}, Cd^{2+} and Hg^{2+} in presence of other alkali, alkaline metal salts.[13] It is evident from the literature that a successful sensor should also indicate selectivity to its corresponding targets.[31] It has become very important and challenging the detection of heavy metals in aqueous systems due to the common co-existence of other metals ions. The synthesized sensor does not show any change in color due to interfering metal ions like alkali, alkaline and other transition metal ions and shown in Fig 3.6 (C). The polymeric hydrogel network captures all metal ions because of the presence of polar groups but naked eye *on-site* inspection cannot be performed. In this study the sensor changes color only when bound with Zn^{2+}, Cd^{2+} and Hg^{2+} separately as well as in the mixture of three metal ions which is a clear advantage for *on-site* inspection. The sensor changes color due to the specific binding of physically engulfed *meta*-BPDM with these metal ions in the presence of other metal ions. It was observed that the binding constant of *meta*-BPDM with Zn^{2+}, Cd^{2+} and Hg^{2+} is relatively higher with other metal ions which are in the order of our earlier report.[13] The main advantage of our synthesized sensor is that *meta*-BPDM ligand does not leach out from the hydrogel matrix after metalation with metal ions in aqueous system or even without metalation during the sensing studies. The color change of the hydrogel could be used to estimate qualitatively Zn^{2+}, Cd^{2+} and Hg^{2+} target ions in the presence of others. The selectivity of the sensor was studied with respect to change in color of hydrogel with time. The sensor cannot be reversed back once metalated as it does not show any effect in acidic or basic conditions. We have taken several solutions of different concentrations of metal ions, Zn^{2+}, Cd^{2+} and Hg^{2+} in a test tube and dipped the small piece of hydrogel into it. The change in color was noted with different intervals of time with respect to the concentration of Zn^{2+}, Cd^{2+} and Hg^{2+} and temperature. It was found that the minimum concentration of 0.5 mg/L of Hg^{2+} ion shows the change in color in 3hrs at 32℃ and in 1 h at 60℃. The time taken to change in color for Zn^{2+} and Cd^{2+} was found to be higher at 32℃ and 60℃ both and shown in Fig.3.6 (D) and Table 3.1.

Table 3.1. Sensing experiment.

Test Solution	**Volume (mL)**	**Weight of the hydrogel used (mg)**	**RPM**	**Time(h) of hydrogel color change at 32˚C**	**Time(h) of hydrogel color change at 60˚C**
H_2O	50	60	120	No change	No change
$ZnCl_2$(1mg/L)	40	60	120	4	2
$HgCl_2$ (0.5 mg/L)	40	60	120	3	1
$CdCl_2$(2 mg/L)	40	60	120	5	3
$ZnCl_2$(1 mg/L) + $HgCl_2$ (0.5 mg/L) + $CdCl_2$(2 mg/L)	40	60	120	3 (which confirms Hg^{2+} presence)	1 (which confirms Hg^{2+} presence)

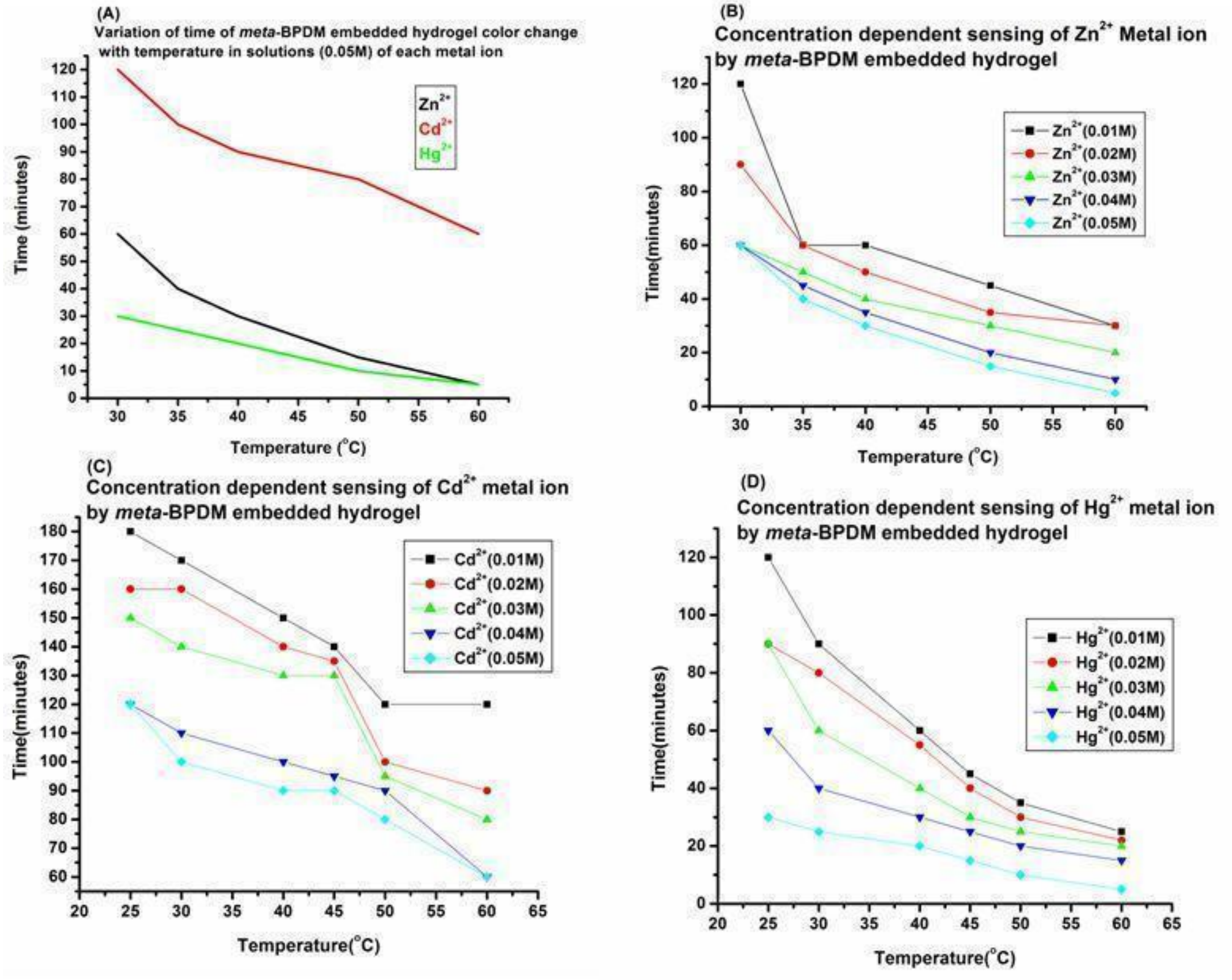


Fig. 3.7 (A) The temperature dependent sensing at constant concentration 0.05M (mol/L^{-1}), i.e. Molarity and (B), (C) and (D), concentration dependent sensing of M^{2+} ion (M= Zn, Cd, Hg) respectively.

Fig. 3.7 (A) depicts the time required for the color change of hydrogel with temperature. It has been noted that at constant metal ion concentration i.e. (0.05M) of each metal ion and at temperature 30℃ the color change of hydrogel occurred at 60 minutes, 120 minutes and 30 minutes for Zn^{2+} , Cd^{2+} and Hg^{2+} respectively. Further at 60 ˚C the sensing was achieved in 5 minutes for

Zn^{2+} and Hg^{2+} and in 60 minutes for Cd^{2+}. The probable cause for the above observations of sensing time for Zn^{2+}, Cd^{2+} and Hg^{2+} can be explained on the basis of binding constants or stability constants of each metal ion with *meta*-BPDM ligand. Zinc and cadmium both have similar properties whereas mercury is somewhat different. As per the theory of Hard-Soft-Acid- base, the *meta*-BPDM contains discrete conjugation pathways and may behave differently than highly conjugated porphyrin analogue and does not come under the category of hard base. Also, the ligand *meta*-BPDM contains sp^2 and sp^3 at *meso* carbons and does contain three pyrrolic –NH involved in conjugation system. It is to be understood that whenever we have diffused electronic conjugation it is to be considered as soft ligand. *Meta*-BPDM binding site are the inner nitrogen's which have conjugated system. Hg^{2+} is soft acid and considering ligand as moderate or soft, the binding of Hg^{2+} is relatively more than Zn^{2+} and Cd^{2+}. Therefore, binding of Hg^{2+} with *meta*-BPDM is taking less time relatively. Fig 3.7 (B), (C) and (D) represent variation of recognition time with temperature of Zn^{2+}, Cd^{2+}, Hg^{2+} respectively at different concentrations. It was found that at low metal ion concentration the hydrogel takes longer time to sense metal ions relative to high metal ion concentrated aqueous solution. The time of sensing decreases on increasing temperature and on increasing metal ion concentration of aqueous solution.

3.3.8. Energy dispersive X-ray analysis (EDX): EDX is an analytical method of elemental analysis related to electron microscopy. Energy Dispersive X-ray spectroscopy (EDX) is a technique that provides information about the abundance of elements and its distribution present in the material. It is based on the emission of characteristic X-rays that indicates the presence of elements within the surface volume of the specimen. EDX of *meta*-BPDM PAM/CMG Zn^{2+} hydrogel was done along with SEM on the same instrument which shows the presence of Zn^{2+} metal ions within the hydrogel. Zn^{2+} is complexed by *meta*-BPDM embedded in hydrogel.[32]

k 2	Ma 16	Take 3	Live 20	Amp 7.6 Time(µs)	Resolutio
V: 0	g: 0	off: 5	Time(s): 0	8 :	n:(eV)

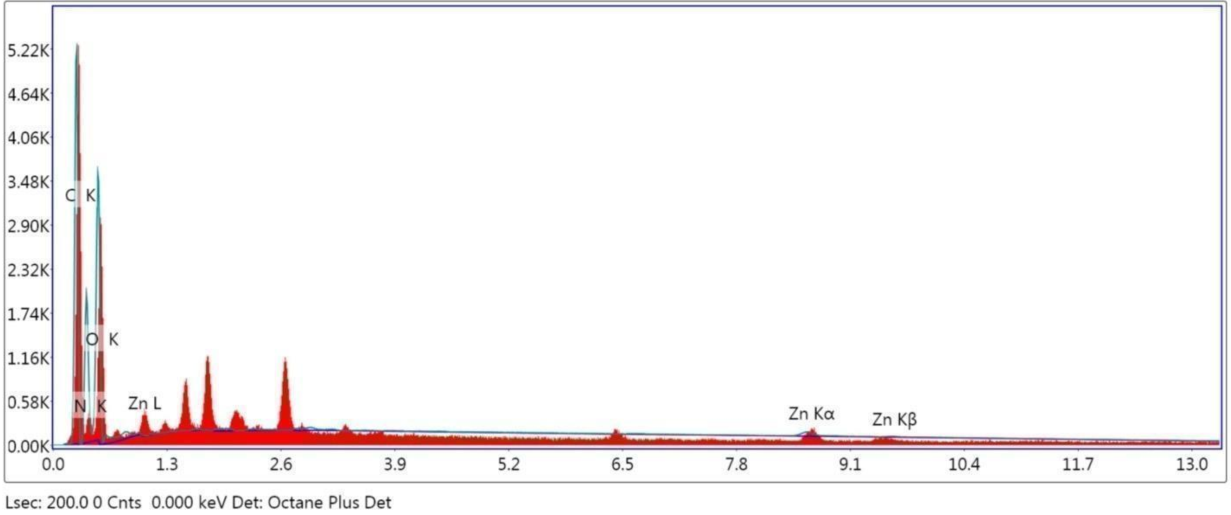


Fig. 3.8 Energy dispersive X-ray analysis *meta*-BPDM-Zn^{2+}- PAM/CMG hydrogel.

3.4 Conclusions

In a nutshell, a polyacrylamide/carboxymethyl guar gum polymeric hydrogel-based metal ion sensor was successfully synthesized by *in situ* incorporation of *meta*-benziporphodimethene using water as solvent. Since *meta*-BPDM is hydrophobic in nature for dissolving this a mixture of acetone and water was used. This hydrogel successfully sensed Zn^{2+}, Cd^{2+} and Hg^{2+}individually and in mixture by showing color change from red to bluish green. The synthesized sensor recognizes Hg^{2+} metal ions upto 0.5 mg/L, which is quite comparable to above the permissible limit. Further, it has also been observed that the sensing time decreases with increase in temperature. This is the first report on polymeric hydrogel can be used for sensing zinc, mercury, cadmium metal ions in aqueous medium. The detection of these metal ions in cells during cell lysis and their estimation and removal from industrial effluents will be discussed in further chapters.

3.5 References:

(1) Chandrangsu, P.; Rensing, C.; Helmann, JD. Metal homeostasis and resistance in bacteria. Nat Rev Microbiol. 2017, 15, 338–350. doi:10.1038/nrmicro.2017.15.

(2) Dean, KM.; Qin, Y.; Palmer, AE.; Visualizing metal ions in cells: an overview of analytical techniques, approaches, and probes. Biochim Biophys Acta. 2012, 1823 (9), 1406–1415. doi:10.1016/j.bbamcr.2012.04.001.

(3) Hossain, SMZ.; Brennan, JD. β-Galactosidase-based colorimetric paper sensor for determination of heavy metals. Anal Chem. 2011, 83, 8772–8778. doi:10.1021/ac202290d.

(4) Xia , S. ; Shen , J.; Wang, J.; et al, Ratiometric fluorescent and colorimetric BODIPY-based sensor for zinc ions in solution and living cells. Sensors Actuators, B Chem. 2018, 258, 1279–1286. doi:10.1016/j.snb.2017.11.129.

(5) Sharma, RK.; Maurya, A.; Kumar, A.; et al. meta-benziporphodimethenes: new cell-imaging porphyrin analogue molecules. ChemistrySelect. 2016, 1, 3502–3509. doi:10.1002/slct.201600812.

(6) Kumar, VV.; Anthony, SP. Silver nanoparticles based selective colorimetric sensor for Cd 2+, Hg2+ and Pb2+ ions: tuning sensitivity and selectivity using co-stabilizing agents. Sensors Actuators, B Chem. 2014, 19, 31–36. doi:10.1016/j.snb.2013.09.089.

(7) Prabhakaran, D.; Nanjo, H.; Matsunaga, H.; Naked eye sensor on polyvinyl chloride platform of chromo-ionophore molecular assemblies: A smart way for the colorimetric sensing of toxic metal ions. Anal Chim Acta. 2007, 601,108–117. doi:10.1016/j.aca.2007.08.032.

(8) Hong , M. ; Lu , X. ; Chen, Y. et al. A novel rhodamine-based colorimetric and fluorescent sensor for Hg2+ in water matrix and living cell. Sensors Actuators, B Chem. 2016, 232, 28– 36. doi:10.1016/j.snb.2016.03.125.

(9) Park, K.; Kim, Y.; Lee, K.J. Fabrication of Metallochromic Dye Functionalized Hydrogel for On-site, Fast, User-friendly Metal-ion Sensing Kit. Macromol. Res. 2020, 28, 580–586. https://doi.org/10.1007/s13233-020-8074-4

(10) Li, W.; Jiang, C.; Lu, S.; Wang, F.; Zhang, Z.; Wei, T.; Chen, Y.; Qiang, J.; Yu, Z.; Chen, X. A hydrogel microsphere-based sensor for dual and highly selective detection of Al3+ and Hg2+, Sensors and Actuators B: Chemical, 2020, 321, 128490, https://doi.org/10.1016/j.snb.2020.128490.

(11) Wan Ngah, W.S.; Hanafiah, M.A.K.M. Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review, Bioresour. Technol. 2088, 99, 3935–3948. doi:10.1016/j.biortech.2007.06.011.

(12) Gupta A.P., Warkar S.G., Synthesis, characterization and swelling properties of poly (Acrylamide-cl-carboxymethylguargum) hydrogels, International J. Pharma Bio Sci. 2015, 6, 516–529.
https://www.researchgate.net/publication/281927604_Synthesis_characterization_and_swelling_properties_of_poly_Acrylamide-cl-carboxymethylguargum_hydrogels (accessed February 20, 2019).

(13) Sharma, R.K.; Gajanan, L.K.; Mehata, M.S.; Hussain, F.; Kumar, A. Synthesis, characterization and fluorescence turn-on behavior of new porphyrin analogue: meta-benziporphodimethenes, Spectrochim. Acta - Part A Mol. Biomol. Spectrosc. 2016, 169, 58–65.

doi:10.1016/j.saa.2016.06.020.

(14) Willard, H.H. ; Merritt, L.L. and J.A. Dean, Instrumental Methods of Analysis, Princeton, 1958.

(15) Hatakeyama, T.; and Liu, Z. Handbook of thermal analysis, John Willey & Sons, New York, USA, 1998.

(16) Coats, A.W.; Redfern, J.P. Thermogravimetric analysis: a review, Analyst. 1963, 88, 906±924.

(17) Inkson, B.J. 2 - scanning electron microscopy (SEM) and transmission electron microscopy (TEM) for materials characterization using nondestructive evaluation (NDE) methods. 2016. 17-43.

(18) Chung, F.H. ; Smith, D.K. Industrial application of x-ray diffraction, Marcel Dekker, New York, 2000.

(19) Bundle, C.R.; Evans, C.A.; Wilson, Jr. S. Encyclopedia of materials characterization, Manning Publications Co. Greenwich, 1992.

(20) Smith, A.L. Applied infrared spectroscopy: fundamentals, techniques and analytical problem solving, John Wiley & Sons, Ltd, 1979.

(21) Griffiths, P.R.; Holmes, C. Handbook of vibrational spectroscopy, Chichester: John Wiley and Sons, 2002.

(22) Pavia, D.L.; Lampman, G.M.; Kriz, G.S. Introduction to spectroscopy, Thomson Learning, Inc., 3rd ed., 2001.

(23) Picollo, M.; Aceto, M.; Vitorino, T. "UV-Vis spectroscopy" Physical Sciences Reviews, 2019, 4, 20180008. https://doi.org/10.1515/psr-2018-0008

(24) Burns RG. Mineralogical applications of crystal field theory. 2nd ed. Cambridge Topics in Mineral Physics and Chemistry Vol. 5. Cambridge: Cambridge University Press, 1993.

(25) Hung, C.H.; Chang, G.F.; Kumar, A. et. al. m-Benziporphodimethene: A new porphyrin analogue fluorescence zinc(II) sensor, Chem. Commun. 2008, 978–980. doi:10.1039/b714412a.

(26) Sharma, R.K.; Maurya, A.; Rajamani, P.; Mehata, M.S.; Kumar, A. meta-Benziporphodimethenes: New Cell-Imaging Porphyrin Analogue Molecules, ChemistrySelect. 2016, 1, 3502–3509. doi:10.1002/slct.201600812.

(27) Chao, Y.C.; Huang, Y.S.; Wang, H.P. ; Fu, S.M.; Huang, C.H.; Liang, Y.C.; Yang, W.C.; Huang, Y.S.; Chang, G.F.; Zan, H.W.; Meng, H.F.; Hung, C.H.; Fu, C.C. An organic hydrogel film with micron-sized pillar array for real-time and indicator-free detection of Zn2+, Org. Electron. 2011, 12, 1899–1902. doi:10.1016/j.orgel.2011.07.001.

(28) Chao, Y.C.; Yeh, S. De.; Zan, H.W.; Chang, G.F.; Meng, H.F.; Hung, C.H.; Meng, T.C.; Hsu, C.S.; Horng, S.F. Real-time and indicator-free detection of aqueous nitric oxide with hydrogel film, Appl. Phys. Lett, 2010, 96, 2008–2011. doi:10.1063/1.3425895.

(29) Ding, B.; Yamazaki, M.; Shiratori, S. Electrospun fibrous polyacrylic acid membrane-based gas sensors, Sensors Actuators, B Chem. 2005, 106, 477–483. doi:10.1016/j.snb.2004.09.010.

(30) Nifiatis, F. Substituent Effects of Porphyrin on Singlet Oxygen Generation Quantum Yields, Open Spectrosc. J. 2011, 5, 1–12. doi:10.2174/1874383801105010001.

(31) Ye, B.F.; Zhao, Y.J.; Cheng, Y.; Li, T.T.; Xie, Z.Y.; Zhao, X.W.; Gu, Z.Z. Colorimetric

photonic hydrogel aptasensor for the screening of heavy metal ions. Nanoscale. 2012, 4, 5998–6003. doi:10.1039/c2nr31601c.

(32) Michalak, I.; Marycz, K.; Basińska, K.; Chojnacka, K.; Using SEM-EDX and ICP-OES to investigate the elemental composition of green macroalga vaucheria sessilis. Sci. World J., 2014, doi:10.1155/2014/891928.

Chapter 4

Detection of Zn^{2+} in *E. coli* Bacterial cells and Zn^{2+}, Cd^{2+} and Hg^{2+} in Industrial Effluents using Modified Polymeric Hydrogels

4.1 Introduction

The monitoring of heavy metal contamination in wastewater is an important step in ensuring human and environmental health. Excess levels of heavy metal may be responsible for several short-term and long-term health effects. The monitoring of Zn^{2+} in living cells and tissue is very crucial owing to its predominant functions as signaling agents to mediate processes such as gene expression, neurotransmission, apoptosis, cell growth and division.[1] Disturbance of zinc homeostasis in human bodies have resulted in health disorders like Alzheimer's disease, diabetes, and several neurodegenerative disorders.[2] Cadmium has detrimental effects on humans causing brain development disorders, chronic inflammation to the heart and kidney, renal dysfunction, and impairing reproductive systems. Hg^{2+} ions have high affinity for thiol groups (-SH) present in proteins and enzymes. Consequently, the presence of Hg^{2+} ions in human bodies leads to the dysfunction of cells in the kidney, brain, and central nervous system. It is highly desirable to monitor Zn^{2+}, Cd^{2+} and Hg^{2+} ions, efficiently and sensitively. Therefore, the need of the hour is to develop a novel probe for the detection of these metal ions in both biological and environmental systems.[3-5] It has been observed that the colorimetric solid sensors render a robust way for sensing and quantification of metal ions with high selectivity and sensitivity.[6] Polymers are the most widely used classes of materials owing to their cost-effectiveness, easy to proceed and their recyclability.[7] In continuation to our last chapter, herein, we further explore the applications of synthesized *m*-BPDM engulfed polymeric hydrogel which provides on-site visual naked-eye detection of spectroscopically silent Zn^{2+}, Cd^{2+}, and Hg^{2+} metal ions in real industrial wastewater and of Zn^{2+} in *E. coli* bacterial cells. The complex formation is Zn^{2+}-*meta* BPDM is stable near physiological pH (7.4) allowing visual naked-eye detection of zinc present in cells via cell lysis.

4.2. Expermental

4.2.1 Materials: Pyrrole, 2,6-difluorobenzaldehyde were distilled prior to use. α, α- dihydroxy-1, 3-diisopropylbenzene were purchased from TCI Chemicals (India) Pvt. Ltd. Boron trifluoride ethyl ether complex, 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) were purchased from SRL Pvt. Ltd. (India) and used as supplied. Silica gel and metal salts were obtained from Merck Germany. Carboxymethyl guar gum was procured from Hindustan Gum and Chemicals Ltd., Bhiwani, Haryana (India). Potassium persulfate ($K_2S_2O_8$) was purchased from Thomas Baker chemicals. Acetone and N, Ń-methylenebisacrylamide (MBA) were purchased from Merck Germany and Acrylamide from SRL. *Escherichia coli* NCIMP-1, phosphate buffer, saline solution (0.9%), Luria broth medium (2%) all reagents were used as obtained. Solvents and all other reagents were used as such without purification. Deionized water was used for aqueous solution preparation.

4.2.2 Synthesis: *m*-BPDM embedded PAM/CMG hydrogels were successfully synthesized using a mixture of acrylamide (2.5 g in 20 mL distilled water) and *m*-BPDM (4 mg in 5 mL acetone: H_2O, 1:1) was taken in a beaker. $K_2S_2O_8$ (0.025 g), N, Ń- methylenebisacrylamide (0.05 g) and carboxymethyl guar gum (0.5g) were added into the same beaker and stirred for 1 hour after that the reaction mixture was transferred into test tubes and placed in the water bath at 60℃ up to gel formation. The obtained red-colored hydrogel was washed with distilled water to remove unreacted chemicals dried first at room temperature and then in the oven to obtain a dried form of hydrogels.

4.2.3 Atomic absorption spectroscopy: The absorption spectra of water containing metal ions were obtained using Spectrum, ZX press 8000 and wavelengths used for Zn^{2+} and Cd^{2+} are 213.9 nm and 228.8 nm respectively. The hydride generation method was used for Hg^{2+} determination using Spectrum SP-HS 100 chemical vapor generator.

4.2.4 UV-visible absorption spectra: UV 1800 Shimadzu Spectrophotometer and PerkinElmer Lambda 750 Spectrometer were used for recording UV-visible absorption spectra of *m*-BPDM and *m*-BPDM embedded hydrogel, respectively.[8,9]

4.2.5 Sensing studies: *m*-BPDM embedded PAM/CMG hydrogels were synthesized successfully and used for the recognition of Zn^{2+} in *E. coli* bacterial cells via cell lysis using SDS detergent (1%) and in real industrial wastewater. Each sensing experiment was performed three times. Each metal ion solution was prepared in deionized water at room temperature.

4.3 Result and Discussion

4.3.1 Synthesis: *m*-BPDM embedded polyacrylamide/carboxymethyl guar gum hydrogel obtained shown in Fig 4.1**.** The uneven and rough surface morphology of PAM/CMG hydrogel remains unaffected upon insertion of *m*-BPDM and on its metalation. The XRD spectra of hydrogel before and after the metalation showed the presence of a broad signal. This may be attributed to the lack of long-range crystallographic order. Hence, it indicated the amorphous nature of cross-linked hydrogel.[9]

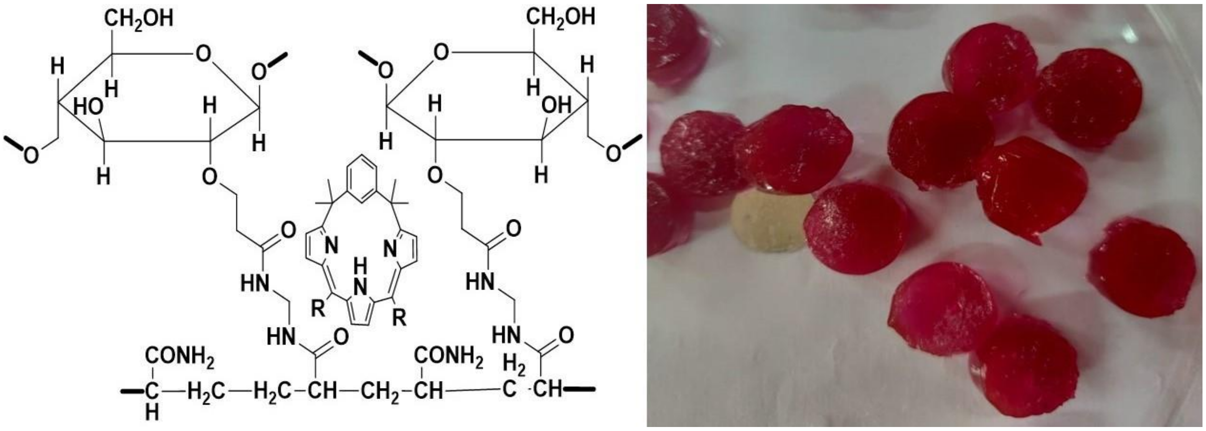


Fig 4.1. Synthesized *m*-BPDM embedded polyacrylamide/carboxymethyl guar gum hydrogel.

4.3.2 UV-visible spectroscopy: UV-visible absorption spectra were used to confirm the synthesis of *m*-BPDM and *m*-BPDM embedded PAM/CMG hydrogel. The UV-visible absorption spectra of the hydrogel are broad due to the discrete conjugated system in *m*-BPDM. High energy Soret band and low energy broad Q bands were observed at 333 nm, and 515 nm, 560 nm respectively. The metalation of hydrogel with Zn^{2+}, Cd^{2+}, Hg^{2+} was observed by the visually detected color change. It was further confirmed by observed shifting in the visible band or low energy Q bands of UV-Visible Spectra from 560 nm to 670 nm. The obtained spectral values matched with our earlier report.[8,9]

4.3.3 Real-time application of *m*-BPDM embedded polyacrylamide/carboxymethyl guar gum hydrogel in sensing Zn^{2+}, Cd^{2+} and Hg^{2+} in the aqueous medium

Free base *m*-BPDM exhibits no background fluorescence while its shows fluorescence *turns on* when bound to Zn^{2+} ions.[8,10-12] A color change from red to bluish-green is observed upon binding with Zn^{2+}, Cd^{2+} and Hg^{2+}.[9] Its sensing properties were explored in an organic solvent viz acetonitrile.[11] In order to sense the environmentally important metal ions present in water, a hydrogel matrix has been utilized owing to its insolubility in water. The hydrogel is a fast response sensing probe, and its stability was examined at different aqueous pH conditions (2, 4, 6, 8, 10) prepared from HCl and NaOH. It was observed that the sensing properties remain unaffected without leaching of *m*-BPDM. Subsequently, it demonstrates that the hydrogel is stable in the physiological environment. The limit of detection with standard deviation is shown in Fig.4.2 and no visual detection was observed below these concentrations. The standard solutions were prepared using their chloride salts maintained at pH 6.5 and temperature 60°C. The observed data is congruent to our last report.[9] All sensing experiments were performed thrice.

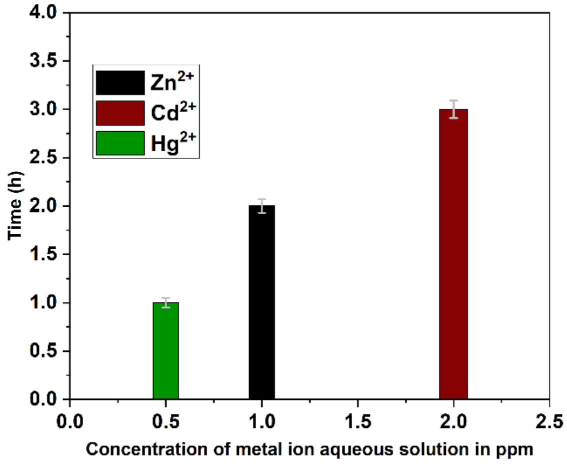


Fig 4.2. Showing limit of detection of Zn^{2+}, Cd^{2+} and Hg^{2+} in their aqueous solution at 60°C.

4.3.4 Selectivity and interference studies: To inspect interferences by non-toxic and other toxic metal ions, a fixed amount of metal salt solution (for instance, 50 ppm) was used to note a change in color. The colorimetric response of *m*-BPDM PAM/CMG hydrogel was analyzed individually using a series of heavy metal ions including Pb^{2+}, Ni^{2+}, Cu^{2+}, Cr^{3+}, Cd^{2+}, Hg^{2+}, Zn^{2+} in the aqueous solution of same metal ion concentration (50 ppm, 120 rpm, RT) to achieve optimum color change shown in Fig 4.3. The selective colorimetric response was observed only with Zn^{2+}, Cd^{2+} and Hg^{2+} (red to bluish-green) solutions. The addition of other heavy metal ions did not exhibit any colorimetric response. To ensure the reproducibility of colorimetric response all experiments were performed 3 times. In order to further, confirm the binding of selective metal ions their absorption spectra were recorded. The spectra displayed a selective red shift of absorption.[8,9] The limit of detection was found to be 0.5 mg/L, 1 mg/L, and 2 mg/L with Hg^{2+}, Zn^{2+} and Cd^{2+}, respectively and found in accordance with our earlier results.[9]

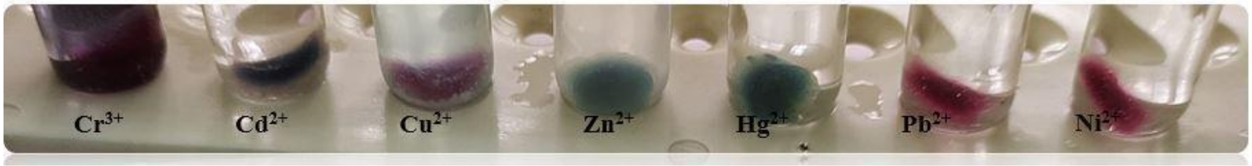


Fig 4.3. Representation of selective colorimetric response.

4.3.5 Sensing behavior with respect to concentration and pH of metal ion solution:

Sensing time or color change of hydrogel in presence of Zn^{2+}, Cd^{2+} and Hg^{2+} in an aqueous medium with concentration and pH were studied. The sensing time was found to be inversely proportional to the concentration of metal ion. This means that the time decreases with an increase in metal ion concentration, in each case, as shown in Fig 4.4. The visual detection limit of 0.5, 1 and 2 ppm of Hg^{2+}, Zn^{2+} and Cd^{2+} respectively was observed. Below these concentrations, no change in hydrogel color was observed at any condition. The pH change does affect detection time considerably, but slightly better results were observed near the 6-7 pH range. This is due to no protonation of acidic functional groups present in the hydrogel matrix as well as no hydroxide formation of metal ions occurring at this range.

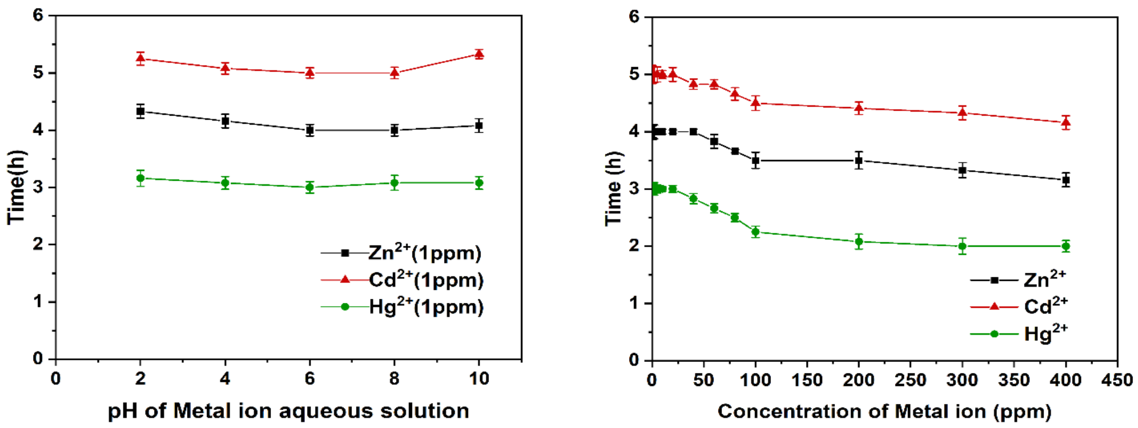


Fig 4.4. Sensing studies with pH and concentration of Zn^{2+}, Cd^{2+} and Hg^{2+} in water.

4.3.6. Sensing in industrial wastewater:

The present study focusses on evaluating the application of the synthesized hydrogel sensor in real wastewater or effluent. The wastewater was collected from Delhi Technological University (DTU), Delhi water treatment plant and industrial effluent in its vicinity. This experiment was done by directly adding hydrogel in wastewater without any pretreatment of effluent. No colorimetric response was observed with the wastewater collected from DTU. Further, the same was analyzed using AAS. The results of AAS revealed that Zn^{2+}, Cd^{2+} and Hg^{2+} ions were absent in the sample. Thus, it may be concluded that the absence of these metal ions in the sample in the detection limit of AAS and sensor produced results in the same manner. Therefore, we can use this sensor to ascertain the presence/absence of these metal ions in water. WHO has suggested a permissible concentration of mercury in drinking water that is 0.001 mg/L and the permissible value of cadmium is 0.003 mg/L. [13] Cadmium and mercury metal ions detectable concentration by this hydrogel are above the WHO permissible limits. The results with industrial effluents whose pH was found to be 6.2 and the change in color is apparent, have been shown in Fig.4.5. The colorimetric response was observed in 2 h, 120 rpm, at RT by simply adding a sensor directly into the collected effluent. These results suggested that there may be the presence of Zn^{2+}, Cd^{2+} or Hg^{2+}

in wastewater. To confirm this, the quantitative determination of Zn^{2+}, Cd^{2+} and Hg^{2+} in the effluent was performed by the AAS technique. The AAS results then confirmed the presence of Zn^{2+} (7 ppm), Cd^{2+} (0.03 ppm) and Hg^{2+} (1.3 ppm). The concentration of zinc and mercury are above the limit of detection of the sensor and therefore, the color change was due to them.

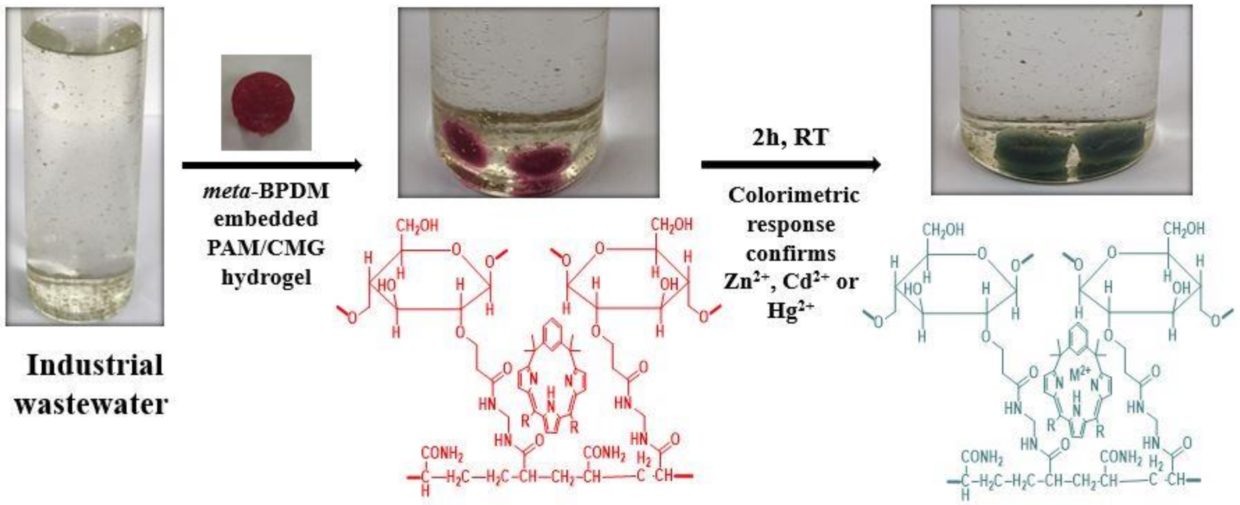


Fig 4.5. Sensing experiment with effluent.

4.3.7 The colorimetric response of *m*-BPDM embedded PAM/CMG hydrogel Sensor to Zn^{2+} present in *E. coli* bacterial cells

Cell lysis was carried out by detergents by incorporating into the cell membrane via solubilizing proteins in the membrane. This results in creating pores within the membrane and eventually full cell lysis. There are many surfactants used for cell lysis including ionic, nonionic and zwitterionic detergents. The choice of surfactants is important as they can affect the speed of cell lysis. Strong ionic detergents like sodium dodecyl sulfate (SDS) can provide cell lysis within seconds by denaturing proteins from the cells.[14]

In this study, we have observed the colorimetric response of *m*-BPDM embedded polyacrylamide/carboxymethyl guar gum hydrogel Sensor to Zn^{2+} present in *E. coli* bacterial cells.

The released Zn^{2+} from *E. coli* bacterial cells via cell lysis absorbed by hydrogel matrix which contain *m*-BPDM ligand and show colorimetric response.

The approach was validated by using *Escherichia coli* NCIMP-1. The cells were cultured in 2% Luria broth medium. Cells were allowed to grow for 24 h at 37 °C. The cells were taken from the medium in a test tube and washed with PBS (2×200 μL). The cells were incubated in saline solution (0.9%, 0.5 mL) and with the zinc metal ion aqueous solution ($ZnCl_2$, 1 ppm, 0.5 mL) for 12 h for visualizing the impact of zinc ions. After incubation the zinc ion-containing solution was removed, cells were washed PBS (2×200 μL). The pretreated cells with zinc ions (1 ppm) in saline solution (0.5 mL) were incubated with the probe (dried crushed hydrogel 1.5 mg) in two test tubes. One of test tubes was with SDS detergent (1%, 0.5 mL) and the other without SDS added at 37 °C. The color of hydrogel was changed from red to bluish-green within 2 h. This indicated the presence of Zn^{2+} in aqueous medium, the release of zinc ion from the cell may be attributed to cell lysis. The test tube without SDS detergent does not show any change in color of the hydrogel as there was no cell lysis (controlled test) and shown in Fig. 4.6. The colorimetric response is specific to Zn^{2+} ions over many biologically relevant mono, divalent metal ions; e.g., Na^{+}, K^{+}, $Ca2^{+}$, Mg^{2+} etc. [8,9]

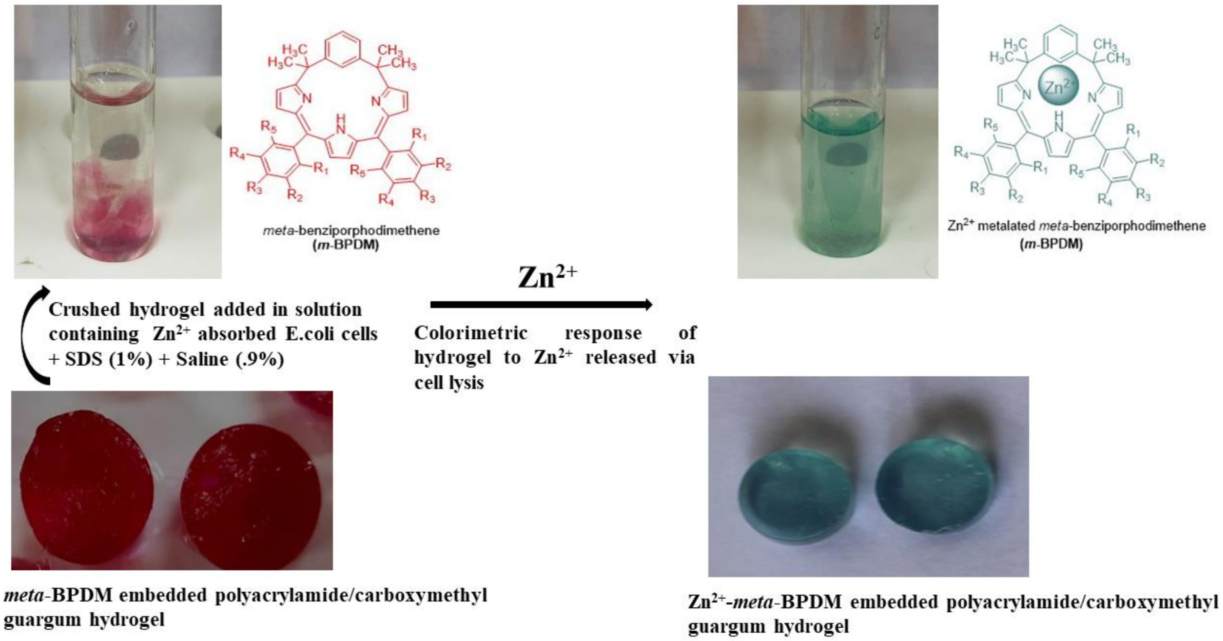


Fig 4.6. Sensing behavior of hydrogel.

The sensor changes color due to the specific binding of physically engulfed ligand *m*-BPDM with zinc metal ions in presence of other metal ions. Hence, in this way, we can detect or sense zinc ions in animal and plant cells. However, the presence of Cd^{2+}, Hg^{2+} can cause interference in sensing of Zn^{2+} in cells but Cd^{2+} and Hg^{2+} are not essential elements for life, therefore, are not present in healthy cells. They are toxic with no known physiological functions and come through absorption from the polluted or contaminated environment Therefore, interference due to them should not occur.[8,9]

4.4 Conclusion

In the present study, *m*-BPDM embedded PAM/CMG polymeric hydrogel-based metal ion sensor was successfully explored for monitoring zinc ions in *E. coli* bacterial cells and Zn^{2+}, Cd^{2+} and Hg^{2+} in the effluent from the industry with high sensitivity and selectivity. The color change was visually detected. This probe is a cost-effective and environmentally friendly on-site real-time colorimetric sensor of Zn^{2+}, Cd^{2+} and Hg^{2+} in the aqueous medium. The sensor provides indicator free detection and opens the possibility for solid-state biosensors specific to Zn^{2+}, Cd^{2+} and Hg^{2+}. The modified hydrogel can be applied in the field of the quantification and removal of Zn^{2+}, Cd^{2+} and Hg^{2+} from the industrial effluent or real wastewater using *m*-BPDM embedded PAM/CMG polymeric hydrogels.

4.5 References

(1) Xia, S.; Shen, J.; Wang, J.; *et. al.* Ratiometric fluorescent and colorimetric BODIPY-based sensor for zinc ions in solution and living cells, Sensors Actuators, B Chem. 2018, 258, 1279–1286. https://doi.org/10.1016/j.snb.2017.11.129.

(2) (a). Sharma, R.K.; Maurya, A.; Kumar, A. *et. al.* *meta*-benziporphodimethenes: New Cell-Imaging Porphyrin Analogue Molecules, ChemistrySelect. 2016, 1, 3502–3509. https://doi.org/10.1002/slct.201600812. (b). Sharma, R.K.; Gajanan, L.K.; Kumar, A. *et. al.* Synthesis, characterization and fluorescence turn-on behavior of new porphyrin analogue: meta -benziporphodimethenes, Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 2016, 169, 58–65. https://doi.org/10.1016/j.saa.2016.06.020.

(3) Kumar, VV.; Anthony, SP.; Silver nanoparticles based selective colorimetric sensor for Cd 2+, Hg2+ and Pb2+ ions: tuning sensitivity and selectivity using co-stabilizing agents, Sensors Actuators, B Chem. 2014, 191, 31–36. doi:10.1016/j.snb.2013.09.089.

(4) Prabhakaran , D.; Nanjo , H.; Matsunaga, H.; Naked eye sensor on polyvinyl chloride platform of chromo-ionophore molecular assemblies: A smart way for the colorimetric sensing of toxic metal ions, Anal Chim Acta. 2007, 601, 108–117. doi:10.1016/j.aca.2007.08.032.

(5) Hong, M.; Lu, X.; Chen, Y.; et al. A novel rhodamine-based colorimetric and fluorescent sensor for Hg2+ in water matrix and living cell, Sensors Actuators, B Chem. 2016, 232, 28– 36. doi:10.1016/j.snb.2016.03.125.

(6) Kaur, P.; Kaur , S.; Mahajan , A.; *et. al.* Highly selective colorimetric sensor for Zn2+ based on hetarylazo derivative, Inorg. Chem. Commun. 2008, 11, 626–629. https://doi.org/10.1016/j.inoche.2008.02.025.

(7) Upama, B.; Devasish, C.; Functionalized graphene oxide quantum dot–PVA hydrogel: a colorimetric sensor for Fe 2+, Co 2+ and Cu 2+ ions, Nanotechnology. 2016, 27, 145501. http://stacks.iop.org/0957-4484/27/i=14/a=145501.

(8) Hung, C.-H.; Chang, G.-F.; Kumar, A.; *et. al.* m-Benziporphodimethene: a new porphyrin analogue fluorescence zinc sensor. Chem. Commun. 2008, 978–980. https://doi.org/10.1039/B714412A.

(9) Chauhan, D.; Kumar, A.; Warkar. S.G.; Synthesis, characterization and metal ions sensing applications of *meta*-benziporphodimethene embedded polyacrylamide/carboxymethyl guargum polymeric hydrogels in water. 2020, 43(7), 991-1002 Environ. Technol. https://doi.org/10.1080/09593330.2020.1812730

(10) Rana, S.; Kumar, A.; Hung, C.-H.; Deshmukh, M.M. Study on the structure, stability and tautomerisms of *meta*-benziporphodimethene and N-Confused isomers containing γ–lactam ring, J. Mol. Struct. 2019, 1187, 138–150. https://doi.org/10.1016/j.molstruc.2019.03.064.

(11) Chang, G.-F.; Kumar, A.; Ching, W.-M. *et. al.* Tetramethyl- *m* -benziporphodimethene and Isomeric α, β-Unsaturated γ-Lactam Embedded N-Confused Tetramethyl- *m* -benziporphodimethenes. Chem. - An Asian J. 2009, 4, 164–173.

https://doi.org/10.1002/asia.200800279.

(12) Jamshaid, M.; Ali Khan, A.; Ahmed, K.; *et. al.* Heavy metal in drinking water, its effect on human health and its treatment techniques - a review. Int. J. Biosci. 2018, 12, 223-240. http://dx.doi.org/10.12692/ijb/12.4.223-240.

(13) Brown, R.B.; Audet, J.; Current techniques for single-cell lysis. J. R. Soc. Interface. 2008, 5 https://doi.org/10.1098/rsif.2008.0009.focus.

(14) Norris, J.L.; Porter, N.A.; Caprioli. R.M.; Mass Spectrometry of Intracellular and Membrane Proteins Using Cleavable Detergents, Anal. Chem. 2003, 75, 6642–6647. https://doi.org/10.1021/ac034802z.

(15) Chauhan, D.; Kumar, A.; Warkar, S. G. Modified polymeric hydrogels for the detection of Zn^{2+} in *E. coli* bacterial cells and Zn^{2+}, Cd^{2+} and Hg^{2+} in industrial effluents, Environmental Technology, 2021, DOI: 10.1080/09593330.2021.1928294

Chapter 5

An efficient adsorbent based on polymeric hydrogel for the removal of Zn^{2+} Cd^{2+} and Hg^{2+} from the wastewater

5.1 Introduction

Heavy metals are not biodegradable therefore their effective removal from aqueous medium is very important for the protection of public health and environment. Efficient techniques are required to monitor certain metal ions from water, mainly the toxic which are harmful even at low concentration.[1,2] Zinc is commonly used in the process of galvanization, alloys, industries, catalyst, textiles. The toxicity due to zinc is uncommon but excess ingestion may cause gastrointestinal distress and diarrhoea. Cadmium is commonly used in batteries, coating, mining alloy, smelting and plastic industry. It causes irritation to the respiratory tract and anaemia. Mercury is one of most toxic heavy metals and non-biodegradable in nature. Major sources of mercury in the environment are such as paint, pulp, fertilizer, thermometers, fluorescent light bulbs etc. It causes genetic defects, nervous system damage, impairment of pulmonary functions, mental retardation, and chest pain.[3] Cd and Hg ions are toxic even at low levels and may lead to death after being accumulated at high concentration in the body. These are toxic, considered carcinogenic. There is great big demand for removal of such toxic heavy metal ions from wastewater.[2] Therefore easy, reliable, selective, and sensitive methods for Zn^{2+}, Cd^{2+} and Hg^{2+} ion monitoring and removal are important for environmental safety and health. Currently, many research reports on industrial wastewater treatment, such as ion exchange membrane method, ammonia desulfurization technology, chemical precipitation, etc., but mostly associated with the disadvantages of complex process, secondary pollution and so on. Among various methods adsorption is the most effective method for removing heavy metal ions with many advantages.[4,5] At present, there are some issues encountered during the preparation of adsorbent materials, such as complex synthesis method and low recovery rate. Therefore, it has become very crucial to use a new adsorbent with simple preparation, high recovery rate and good adsorption capacity. The adsorption process involves three main stages: heavy metal ions permeate via convection diffusion from wastewater to the adsorbent surface; heavy metal ions adsorb on the surface of the adsorbent; and continue to migrate into the adsorbent interior.[6] Adsorbent involves the binding or chemical reaction with itself and does not cause secondary pollution to the sewage. The operation process is very simple, friendly to the environment, and the removal efficiency of heavy metal ions is high and cost effective.

This chapter presents a robust and cost-effective approach for removal of Zn^{2+}, Cd^{2+} and Hg^{2+} from aqueous solution using *meta*-BPDM embedded PAM/CMG hydrogel in pellet form. The sorption, adsorption kinetics and isotherm studies of this hydrogel has been reported here which was not mentioned so far. The presence of polar hydrophilic functional groups (-OH, NH_2, -COOH) in polyacrylamide/carboxymethyl guar gum and porphyrin analogue *meta*-BPDM act as binding sites via polar or electrostatic interaction. It has made *meta*-BPDM embedded PAM/CMG hydrogel an effective sorbent for Zn^{2+}, Cd^{2+} and Hg^{2+} in wastewater treatment. All these indicate that the hydrogel is effective adsorbent, has a crucial role in the treatment of effluents and the protection of ecological environment.

5.2 Experimental

5.2.1 Materials

Pyrrole, 2,6-Difluorobenzaldehyde and α, α dihydroxy-1, 3-diisopropylbenzene were purchased from TCI chemicals (India) Pvt. Ltd. Silica gel, Acetone, N, Ń-methylenebisacrylamide (MBA) and metal salts were obtained from Merck Germany. Boron trifluoride ethyl ether complex, 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) were obtained from SRL Pvt. Ltd. (India). Carboxymethyl guar gum was procured from Hindustan

Gum and Chemicals Ltd., Bhiwani, Haryana (India). Potassium persulfate ($K_2S_2O_8$) was purchased from Thomas Baker chemicals and Acrylamide from SRL. Deionized water was used for synthesis and for all metal ions aqueous solution preparation.

5.2.2 Synthesis *meta*-BPDM embedded polyacrylamide/carboxymethyl guar gum and polyacrylamide/carboxymethyl guar gum hydrogel were synthesized according to previous reports.[7] The digital photo of hydrogel is shown in Fig 5.1.

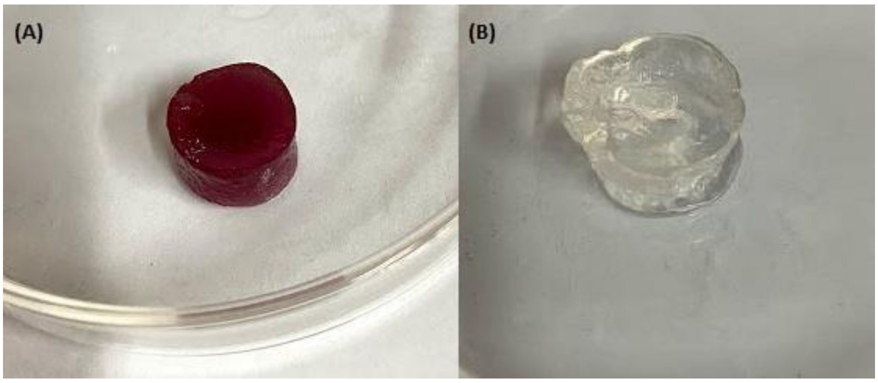


Figure 5.1. (A) *meta*-BPDM PAM/CMG hydrogel, (B) PAM/CMG hydrogel.

5.2.3 Instrumentation: The synthesized hydrogel and metalated hydrogel were characterized using Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), Scanning electron microscopy (SEM). IR-spectrum was collected using KBr pellets containing 1% sample from 4000 cm^{-1} to 400 cm^{-1} (NICOLET 380), the surface morphology of hydrogel was observed by using SEM (JEOL JSM-6610LV) after coated with conductive film of platinum. The thermal stability of hydrogels was investigated by TGA (Perkin Elmer TGA 4000.). The sample was heated at 10 ℃/min from 80 ℃ to 800 ℃ under the N_2 atmosphere. The initial and residual concentration of metal ions in water were measured using ICP-MS (Perkin Elmer 300X) and AAS (ZX press 8000).

5.2.4 Selectivity studies: In a 50 mL solution of all metal ions with pH 6.5 and initial concentration 500 ppm, 0.082g hydrogel pellet was added. The solution was shaken with 250 rpm at room temperature for 5 h. The equilibrium concentration of all metal ions was observed using AAS. The adsorption selectivity was also compared between Blank hydrogel i.e., PAM/CMG hydrogel and *meta*-BPDM embedded PAM/CMG hydrogel. Removal percentage was calculated for each metal ion.

5.2.5 Adsorption experiments: Batch sorption of Zn^{2+}, Cd^{2+} and Hg^{2+} by hydrogel (0.082g) were studied at room temperature (about 28°C) using 10 mL of heavy metal ion aqueous solution. Analytical grade chloride salts of Zn^{2+}, Cd^{2+} and Hg^{2+} were used to prepare standard stock solutions in deionized water. Adsorption experiment was performed using a diluted stock solution at room temperature. The desired pH was adjusted using HCl (0.1N) and NaOH (0.1N). The effect of initial metal ion concentration, pH and contact time were studied. The results obtained from these studies were used to demonstrate the optimum conditions for maximum removal from aqueous solutions.

5.2.6 Removal of Zn^{2+}, Cd^{2+} and Hg^{2+} from industrial wastewater: 0.082g hydrogel pellet was suspended in 10 mL of industrial wastewater (collected from industries nearby DTU, Delhi). The pH of the mixture was adjusted to 6.5 and stirred for 4 h (250 rpm) at room temperature to obtain equilibrium. The initial and remaining concentration after adsorption of Zn^{2+}, Cd^{2+} and Hg^{2+} in the sample were determined by AAS.

5.3 Result and Discussion

5.3.1 Synthesis and Characterization of blank, *meta*-BPDM embedded and metalated *meta*-BPDM embedded polyacrylamide/ carboxymethyl hydrogel:

Fig 5.2 (A). Showing the Fourier-transform infrared spectroscopy (FTIR) spectrums of *meta*-BPDM embedded polyacrylamide/ carboxymethyl hydrogel, Zn^{2+}- *meta*-BPDM PAM/CMG, Cd^{2+}-*meta*-BPDM PAM/CMG, Hg^{2+}- *meta*-BPDM PAM/CMG, Zn^{2+} Cd^{2+} and Hg^{2+}-*meta*-BPDM PAM/CMG. The absorption bands at 3200-3300 cm^{-1} were related to -OH and N-H stretching and N-H and O-H overlapped. The bands at 2730 cm^{-1} are due to saturated C-H and 2800 cm^{-1} unsaturated C-H stretching mode. The peak at 1050 cm^{-1} corresponds to C-N stretching, 1250 cm^{-1} represents C-O bending ,1450 cm^{-1} related to O-H bending ,1400 cm^{-1} corresponds to C-O-C stretching vibration in the CMG. The strong peak at 1720 cm^{-1} corresponded to C=O groups.[8]

Thermogravimetric analysis was used to investigate thermal properties of hydrogel. Similar degradation pattern was observed with all hydrogels whereas in case of Zn^{2+} and Cd^{2+} metalated hydrogel decomposition is slightly different that may be due to binding coefficient of these two metal ions with *meta*-BPDM. Overall, it has been observed that insertion of *meta*-BPDM and its metalation do not affect thermal stability of the PAM/CMG hydrogel considerably. Which indicates that there is no chemical interaction between them. The weight loss up to 100 ℃ was owing to water evaporation from the hydrogel. The hydrogel undergoes sharp weight loss in the temperature range of 250-350 ℃ due to the degradation of -OH and carboxymethyl group. The weight loss from 350-500 ℃ is due to decomposition of the polymer backbone, crosslinking, and amide groups. The final weight loss is due to degradation of the organic backbone, C-O-C *meta*-BPDM ring. The overall analysis depicts that the hydrogel sample had adequate thermal stability. Fig 5.2. (B)

Surface properties were analysed using scanning electron microscopy; the morphology was found to be irregular, porous which provides effective adsorption for the heavy metals. The morphology is presented in Fig.5.2 (C), (a), present surface microphotograph of *meta*-BPDM PAM/CMG hydrogel and Fig. 5.2 (C), (b), showing of Zn^{2+}, Cd^{2+} and Hg^{2+} metal-loaded *meta*-BPDM PAM/CMG hydrogel. The surface morphology slightly changes after adsorption that may be attributed to conformation change on metalation. Overall, no chemical change in morphology is observed on metalation which indicates that there is physical interaction between metal loaded *meta*-BPDM and hydrogel.

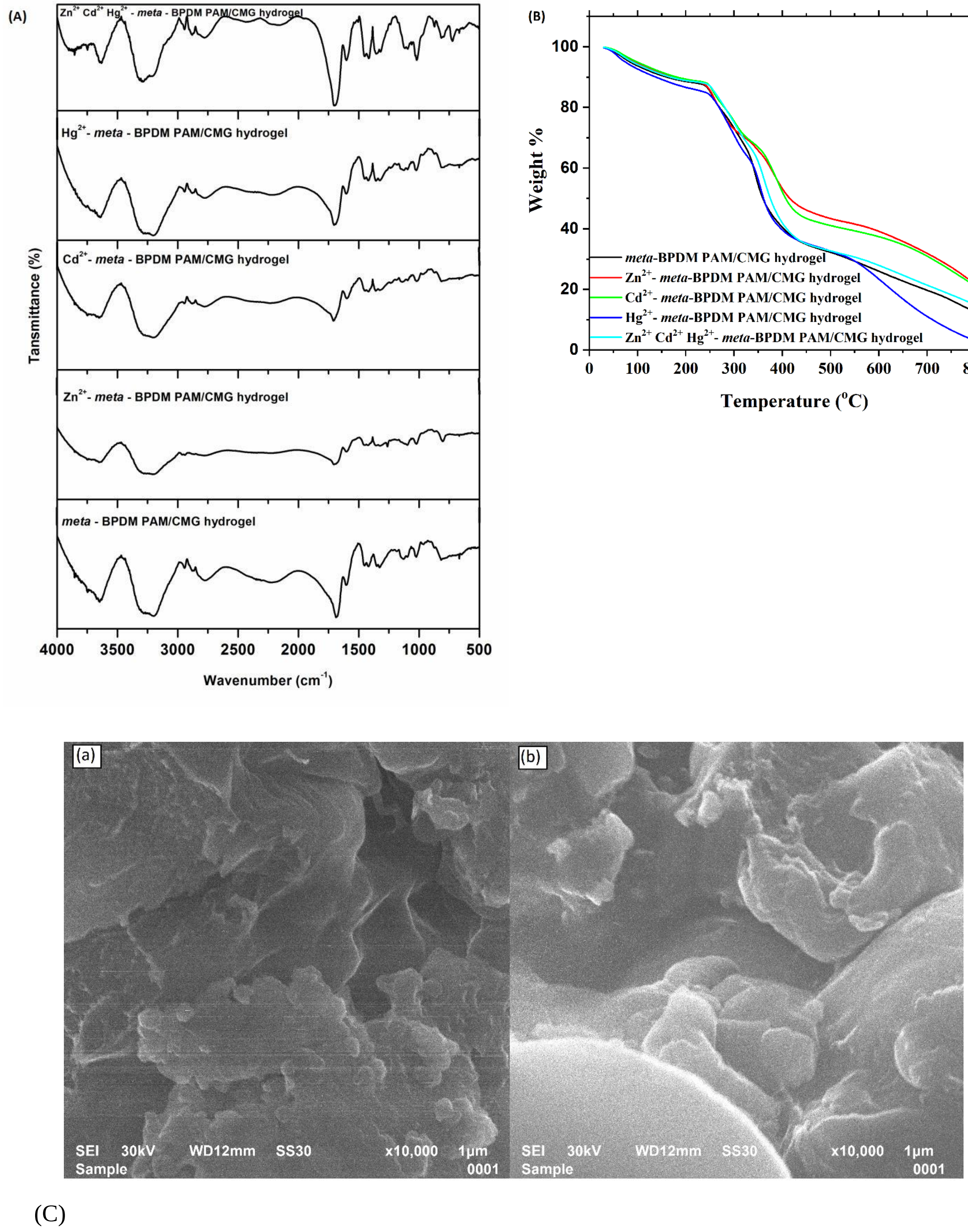


Figure 5.2. (A) FTIR Spectra of hydrogels, (B) TGA Curves of hydrogels, (C) Surface microphotographs of hydrogels.

5.3.2 Selectivity/competitive studies: The industrial discharge usually contains multiple metal ions therefore it has become important to study the competitive removal of metal ions. Selective removal of Zn^{2+}, Cd^{2+} and Hg^{2+} was observed in a mixture of multiple metal ions Fig 5.3. It can be attributed to specific interaction of Zn^{2+}, Cd^{2+} and Hg^{2+} with embedded *meta*-BPDM or active functional groups in the hydrogel. Other than *meta*-BPDM a large number of $-NH_2$, -OH, -COOH, and $-CONH_2$ functional groups of PAM/CMG hydrogel can act as binding sites for the Zn^{2+}, Cd^{2+} and Hg^{2+}. Functional groups having nitrogen are selectively involved in Hg^{2+} binding. Therefore, adsorption isotherm and kinetics was studied with respect to only Zn^{2+}, Cd^{2+} and Hg^{2+} removal. The aqueous solutions of all metal ions of required concentrations were prepared using their chloride salts in deionized water. The higher affinity of hydrogel among Zn^{2+}, Cd^{2+} and Hg^{2+} was found to be with respect to Hg^{2+}. This can be supported by hard soft acid base theory towards active functional groups having nitrogen and *meta*-BPDM. The reason for higher chelation of Hg^{2+} is due to its soft nature preferably binds with soft base $-NH_2$, -C=N, =N. The presence of interfering ions would affect the uptake of target ions but not appreciable, however the hydrogel can be used for the removal of Zn^{2+}, Cd^{2+} and Hg^{2+}. This hydrogel is better suited to Zn^{2+}, Cd^{2+} and Hg^{2+} due to higher binding constants of embedded *meta*-BPDM ligands with these metal ions.[7,9,10]

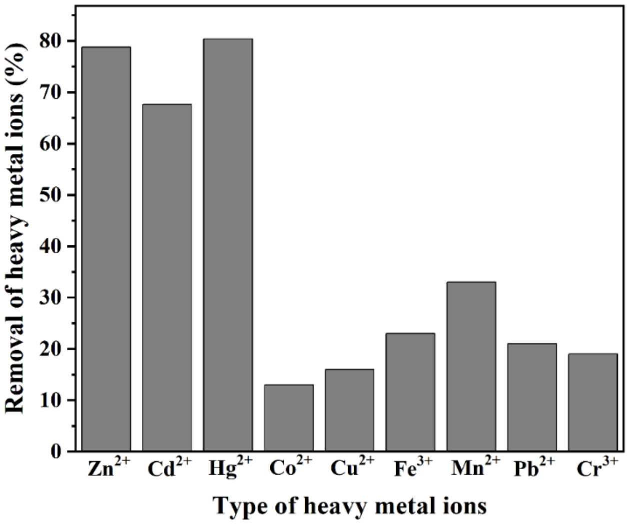


Figure 5.3. Percentage removal of heavy metal ions using *meta*-BPDM PAM/CMG hydrogel (volume for each metal ion solution 10 mL, weight of hydrogel 82mg, initial metal ion concentration C_o, 500 ppm at RT pH 6.5 and stirred magnetically at 250 rpm for 24 h).

5.3.3 Individual heavy metal ion removal from aqueous solution (Non-Competitive Environment):

Non-competitive adsorption was studied using aqueous solution containing only one type of metal ion. The amount of Zn^{2+}, Cd^{2+} and Hg^{2+} removed by non-competitive adsorption is more than that can be achieved by competitive adsorption. The selective interaction between hydrogel and Zn^{2+}, Cd^{2+} and Hg^{2+} in water dominated. The aqueous solutions of Zn^{2+}, Cd^{2+} and Hg^{2+} of required concentrations were prepared using their chloride salts in deionized water. All experiments were carried out at pH 6.5 initially adjusted using HCL and NaOH, where the maximum adsorption was obtained. The weight of dry hydrogel pellets was 0.082g uniformly in all batch experiments. The hydrogel was immersed in V 10 mL of aqueous solution with initial metal ion concentration C_o, 500 ppm at RT and stirred magnetically at 250 rpm for 24 h.

Metal absorbed or equilibrium adsorption capacity (mg/g), $q_e = \frac{V\,(C_o - C_e)}{W}$

Removal efficiency or Sorption % = $\frac{(C_o - C_e)}{C_o} \times 100$

W= 82.0 mg dosage of dried hydrogel, $q_e(mg/g)$ and $C_e(ppm)$ is the amount adsorbed and concentration left at equilibrium respectively[8].

Table 5.1. Uptake of zinc, cadmium and mercury by *meta*-BPDM PAM/CMG hydrogel.

Metal ion	$C_o(ppm)$	$C_e(ppm)$	$q_e(mg/g)$	% Removal
Zn^{2+}	500	106	48.0	78.8
Cd^{2+}	500	162	41.21	67.6
Hg^{2+}	500	98	49.02	80.4

Table 5.2. Uptake of zinc, cadmium, and mercury by PAM/CMG (blank) hydrogel.

Metal ion	$C_o(ppm)$	$C_e(ppm)$	$q_e(mg/g)$	% Removal
Zn^{2+}	500	265	28.43	47
Cd^{2+}	500	235	32.06	53
Hg^{2+}	500	280	26.62	26.62

The absorption capacity and removal percentage of Zn^{2+}, Cd^{2+} and Hg^{2+} using *meta*-BPDM embedded PAM/CMG hydrogel was found to be higher than PAM/CMG hydrogel (blank).

5.3.4 Effect of initial metal ion concentration and contact time. The adsorption behaviour of hydrogel was studied in the batch experiment. Removal efficiency is significantly affected by the initial metal ion concentration, with increase in initial concentration of Zn^{2+}, Cd^{2+} and Hg^{2+} q_e also increases due to higher chances of collision between metal ions. Which results in utilization of all active adsorption sites on adsorbent. At high C_o the number of metal ions are higher than the available vacant sites in the hydrogel. Therefore, removal efficiency depends on the initial metal ion concentration. The maximum adsorption (q_e) at equilibrium was 47.67, 40.89 and 48.64 mg/g for Zn^{2+}, Cd^{2+} and Hg^{2+} respectively at RT, pH 6.5, dry hydrogel W 82mg, volume of aqueous solution V 10 mL, Time 12 h, rpm 250, C_o (50, 150, 250, 300, 400, 500, 600,700 ppm), $C_e =$ concentration at equilibrium. Fig 5.4 (A)

$$q_e = \frac{V\,(C_o - C_e)}{W}$$

Contact time is a very important factor for the determination of equilibrium point. Which can be used to study the kinetics of the adsorption process. The supernatants obtained after the hydrogel treatment were acidified and analysed by ICP-MS as an independent verification at each time interval (10, 20, 30, 60, 120, 180, 240, 300, 360, 420, 480, 720 840 min). The decrease in concentration after each interval can be explained by the ability of *meta*-BPDM PAM/CMG hydrogel to bind with metal ions. These plots with time indicate that the residual concentration of metal ions becomes asymptotic showing no appreciable change in the residual concentration of metal ions after 360 min in the case of mercury, 480 min in the case of zinc and 720 min in the case of cadmium. These represent the time at which equilibrium has been attained. q_t and C_t are the amount adsorbed (mg/g), residual concentration at time interval t respectively[3]. Fig 5.4 (B)

$$q_t = \frac{V\,(C_o - C_t)}{W}$$

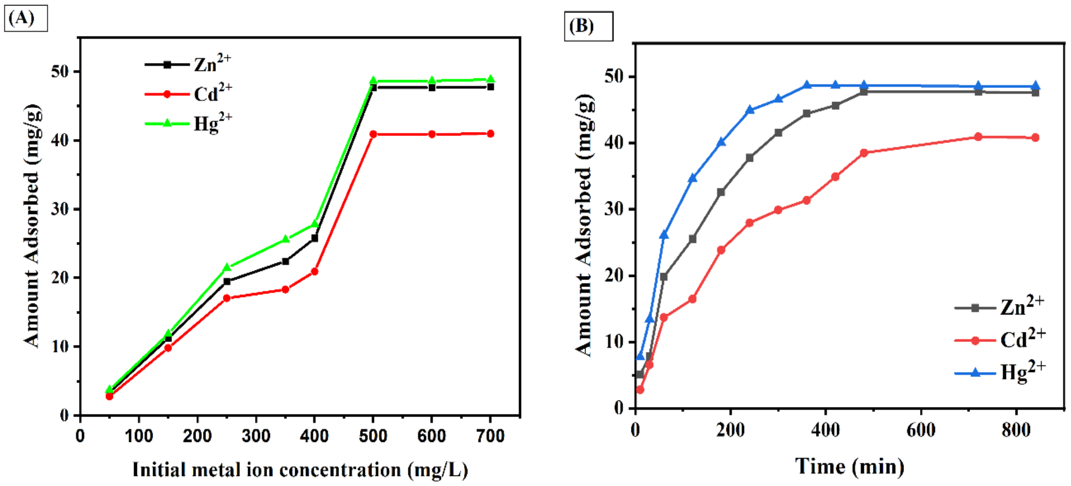


Figure 5.4. Effect of initial metal ion concentration (A) and contact time (B) on adsorption of Zn^{2+}, Cd^{2+} and Hg^{2+} ions.

5.3.5 Effect of pH: The effect of pH plays the most important role in determining the parameters controlling removal of heavy metals from aqueous solutions. It affects the ionization or dissociation and precipitation of adsorbate and surface properties of the adsorbent. The effect pH is more prominent when both adsorbate and adsorbent are charged or polar species. The pH of the solution affects the adsorption efficiency by protonating the polar functional group in the sorbent and precipitating metal ions as hydroxide or oxides. Hydrogen's ions may compete with metal ions for the active site on adsorbent at lower pH as well as adsorption sites that get protonated.[3,8] The pH effect on the absorption of Zn^{2+}, Cd^{2+} and Hg^{2+} was studied in a pH range from 2 to 9. At $pH > 6$ the metal hydroxides would precipitate in aqueous solution that may affect the accuracy of results. The optimum pH was found to be 6.5 corresponds to maximum removal and above this metal hydroxide precipitation occurs. The observed results are displayed in Fig.5.5

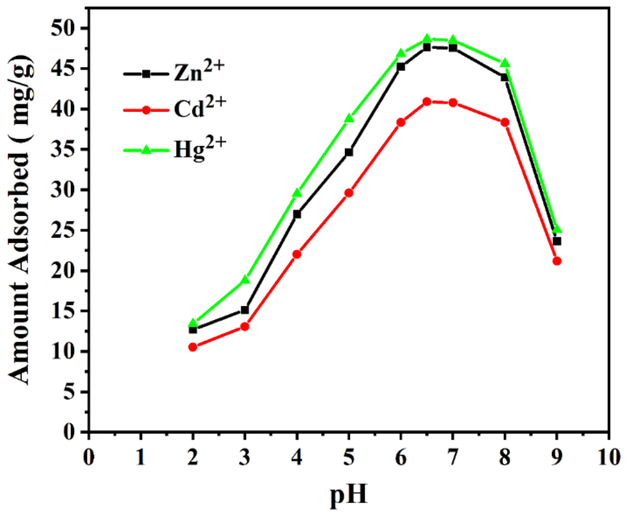


Figure 5.5 Effect of pH on adsorption of zinc, cadmium and mercury. C_o= 500 ppm, W= 82.0 mg, V= 10 mL, RT, 250 rpm.

5.3.6 Adsorption Isotherm studies:

Adsorption isotherms represent how adsorbate and adsorbent molecules interact with each other, so are important in optimizing the utility of adsorbents. The obtained results were analysed by the Langmuir and Freundlich models. The Langmuir model assumes the adsorbent is having structurally homogeneous identical sorption sites with similar energies. The linear form of Langmuir equation is given by

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{bQ_o\,C_e}$$

Q_o and b are the Langmuir constants.^{3,8,12} The linearized form of the isotherm and high value of correlation coefficient (R^2) suggest that the adsorption follows the Langmuir model which indicates chemisorption. Fig 5.6 (A)

The logarithmic equation of Freundlich model is given by

$$log\ q_e \ = \ log\ K_F \ + \left(\frac{1}{n}\right) log\ C_e$$

where K_F and n are the adsorption capacity and adsorption intensity related Freundlich constants respectively.[3,8,13] Fig 5.6 (B) showing plots of $log\, q_e$ against $log\, C_e$ for the adsorption of zinc, cadmium and mercury. It is clearly visible that the data is not fitting very well in the Freundlich isotherm which indicates physisorption. Fig 5.6 (B)

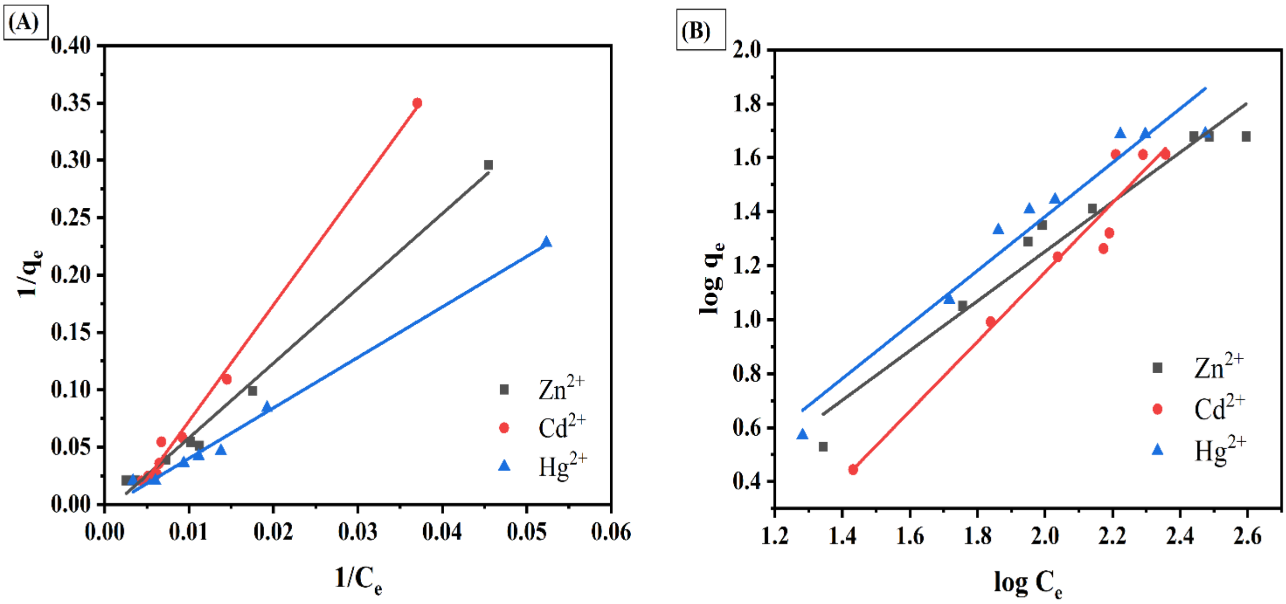


Figure 5.6. Langmuir (A), Freundlich (B) isotherm model for Zn^{2+}, Cd^{2+} and Hg^{2+} ions adsorption.

5.3.7 Adsorption kinetics: The pseudo-first and second order model is the most common for solid liquid interaction and was applied to describe the sorption process. t is contact time, q_t and q_e are absorption capacity at time t and at equilibrium, k_1 and k_2 are rate constants for pseudo-first and second order reactions. The Pseudo-first order model considers rate of adsorption as controlled by mass transfer and diffusion whereas in case of the pseudo-second order it considers chemisorption is the rate controlling step.[8,13]

Absorption capacity, $q_t = \frac{V(C_o - C_t)}{W}$

$$log\ (q_e - q_t) = log\ q_e - \frac{k_1}{2.303} t \qquad \text{Pseudo-first order}$$

$$\frac{t}{q_t} = \frac{1}{k_2\, q_e{}^2} + \frac{t}{q_e} \qquad \text{Pseudo-second order}$$

The calculated q_e values of the pseudo second order match closely more with experimental as well as correlation coefficient (R^2) was higher (Table 5.3). Therefore, results obtained from a pseudo second order kinetic model better described the adsorption by hydrogel indicating chemisorption adsorption process Fig 5.7 (A) and (B).

Table 5.3. Kinetic parameters for the adsorption of Zn^{2+}, Cd^{2+} and Hg^{2+} ions

	Pseudo-first order			Pseudo-second order		
Metal ion	k_1	q_{e1}	R^2	k_2	q_{e2}	R^2
Zn^{2+}	0.00663	43.74	0.9539	0.00011	51.42	0.9929
Cd^{2+}	0.00619	52.54	0.9432	0.00009	42.52	0.9950
Hg^{2+}	0.00838	25.02	0.7451	0.00028	53.09	0.9975

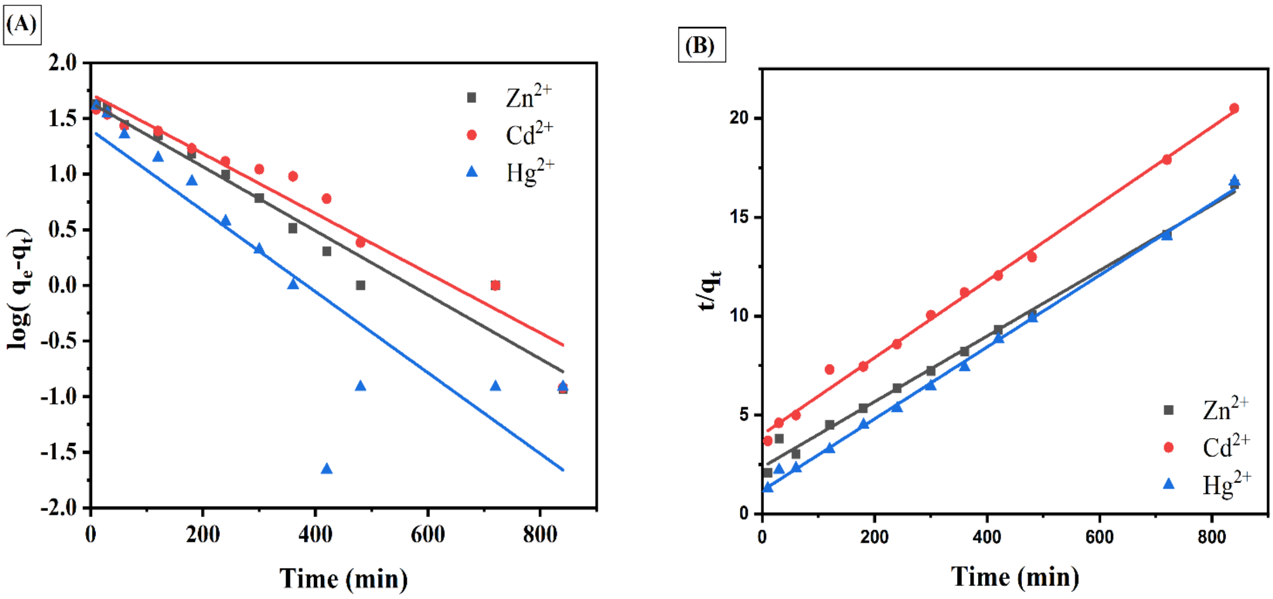


Figure 5.7. Pseudo-first order (A) and pseudo-second order (B) kinetic model on Zn^{2+}, Cd^{2+} and Hg^{2+} ions adsorption.

5.3.8 Removal of Zn^{2+} Cd^{2+} and Hg^{2+} from real wastewater: In order to assess the feasibility of the *meta*-BPDM PAM/CMG hydrogel for the removal of Zn^{2+}, Cd^{2+} and Hg^{2+} water. A real wastewater collection is collected from the vicinity of some industries nearby DTU, Delhi and other industrial areas of Delhi, India. ICP-MS showed very less amount of detectable Zn^{2+}, Cd^{2+} and Hg^{2+} (less than 3 ppm) in the collected waste water so chlorides salts of metal ions were added to simulate contaminated water (500ppm). The water sample was transferred into the conical tubes at pH 6.5, RT, C_o 500 ppm, and a meta-BPDM PAM/CMG hydrogel-based sensor was added into the tubes, allowed to soak for 1 day. After soaking the supernatant solutions were collected and acidified using 1% HNO_3 for ICP-MS analysis. The concentrations in the supernatant were found to be decreased from 500 ppm to 113, 170, 102 ppm for Zn^{2+}, Cd^{2+} and Hg^{2+} respectively after the gel treatment. The results suggest that the hydrogel was capable of removing these metal ions from natural water sources.[14] Fig 5.8 depicts the hydrogel removal efficiency with respect to Zn^{2+}, Cd^{2+} and Hg^{2+} in water. Removal $\% = \frac{(C_o - C_e)}{C_o} \times 100$

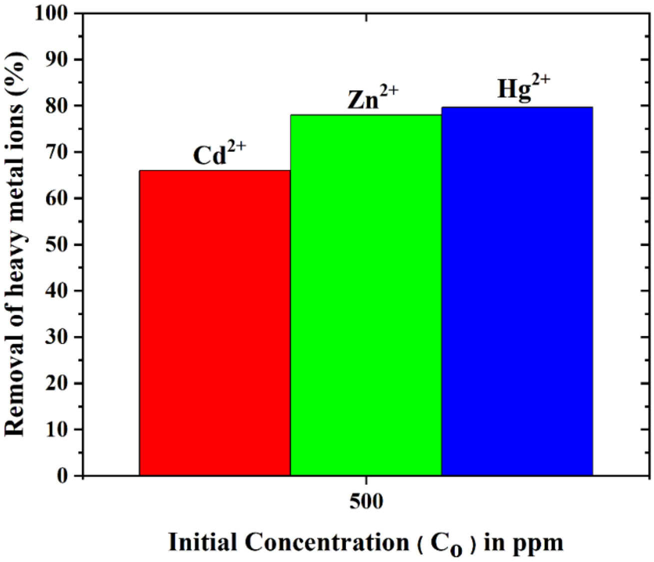


Figure 5.8. Removal (%) of Zn^{2+}, Cd^{2+} and Hg^{2+} by hydrogel from industrial effluents at RT.

5.4 Conclusion: The porous structure of modified copolymer-based hydrogel was beneficial for permeation of metal ions into it. The optimum pH was found to be 6.5 and Zn^{2+}, Cd^{2+} and Hg^{2+} achieved adsorption equilibrium within 12 h. The order of adsorption in the multicomponent system was found to be $Hg^{2+} > Zn^{2+} > Cd^{2+}$. The adsorption data fit very well to the Langmuir adsorption isotherm model and pseudo second order equation. It is found that the adsorption of Hg^{2+} is better than Zn^{2+} and Cd^{2+} under similar conditions due to difference in affinity or binding constants sequence $Hg^{2+} > Zn^{2+} > Cd^{2+}$ with the incorporated *meta*-BPDM in the PAM/CMG hydrogel. The obtained result establishes a suitable method with promising applications for efficient removal of Zn^{2+}, Cd^{2+} and Hg^{2+} from their aqueous solution

5.5 References

(1) Jin, L.; Bai, R. Mechanisms of lead adsorption on chitosan/PVA hydrogel beads. Langmuir 2002, 18, 9765–9770. https://doi.org/10.1021/la025917l.

(2) Karbarz, M.; Khalil, AM.; Wolowicz, K.; Kaniewska, K.; Romanski, J.; Stojek , Z. Efficient removal of cadmium and lead ions from water by hydrogels modified with cystine. J. Environ. Chem. Eng. 2018, 6, 3962–3970. https://doi.org/10.1016/j.jece.2018.05.054

(3) Meena, AK.; Mishra, GK.; Rai, PK.; Rajagopal, C.; Nagar, PN. Removal of heavy metal ions from aqueous solutions using carbon aerogel as an adsorbent. J. Hazard. Mater. 2005, 122 ,161–170. https://doi.org/10.1016/j.jhazmat.2005.03.024

(4) Mu, R.; Liu, B.; Chen, X.; Wang, N.; Yang, J. Hydrogel adsorbent in industrial wastewater treatment and ecological environment protection, Environmental Technology & Innovation, 2020, 20, 101107, https://doi.org/10.1016/j.eti.2020.101107.

(5) Wang, G.; Wang, S.; Sun, W. et. al. Synthesis of a novel illite@carbon nanocomposite adsorbent for removal of Cr (VI) from wastewater, J. Environ. Sci. 2017, 57 (07), 64–73.

(6) Bhargava, S.; Uma, V. Rapid extraction of Cu (II) heavy metal from industrial waste water by using silver nanoparticles anchored with novel schiff base. Sep. ence Technol. 2018, 54 (7) ,1–12.

(7) Chauhan, D.; Kumar, A.; Warkar, S.G.; Synthesis, characterization and metal ions sensing applications of *meta*-benziporphodimethene embedded polyacrylamide/carboxymethyl guargum polymeric hydrogels in water. 2020, 43:7, 991-1002 Environ. Technol. https://doi.org/10.1080/09593330.2020.1812730

(8) Zhao, B.; Jiang, H.; Lin, Z.; Xu, S.; Xie, J.; Zhang, A. Preparation of acrylamide/acrylic acid cellulose hydrogels for the adsorption of heavy metal ions. Carbohydr. Polym. 2019, 224,

115022. https://doi.org/10.1016/j.carbpol.2019.115022

(9) Chauhan, D.; Kumar, A.; Warkar, SG.; Modified Polymeric Hydrogels for the Detection of Zn2+ in E. coli Bacterial cells and Zn2+, Cd2+ and Hg2+ in Industrial Effluents. Environ.Technol. (United Kingdom), (2021) DOI: 10.1080/09593330.2021.1928294

(10) Lone, S.; Yoon, DH.; Lee, H.; Cheong, IW.; Gelatin-chitosan hydrogel particles for efficient removal of Hg(ii) from wastewater. Environ. Sci. Water Res. Technol. 2019, 5, 83–90. https://doi.org/10.1039/c8ew00678d

(11) Wang, F.; Zheng, Y.; Zhu, Y.; Wang, A. Preparation of chitosan-g-poly (vinylimidazole-co-2-acrylamido-2-methyl propane sulfonic acid) granular hydrogel for selective adsorption of Hg2+. Water. Air. Soil Pollut. 2016, 227. https://doi.org/10.1007/s11270-016-2812-4

(12) Ozay, O.; Ekici, S.; Baran, Y.; Aktas, N.; Sahiner, N. Removal of toxic metal ions with magnetic hydrogels. Water Res. 2009, 43, 4403–4411. https://doi.org/10.1016/j.watres.2009.06.058

(13) Gupta, VK.; Jain, CK.; Ali, I..; Sharma, M.; Saini, VK. Removal of cadmium and nickel from wastewater using bagasse fly ash - A sugar industry waste. Water Res. 2003, 37, 4038–4044. https://doi.org/10.1016/S0043-1354(03)00292-6

(14) Najafi, M.; Rostamian, R.; Rafati, AA. chemically modified silica gel with thiol group as an adsorbent for retention of some toxic soft metal ions from water and industrial effluent. Chem. Eng. J. 2011, 168, 426–432. https://doi.org/10.1016/j.cej.2010.12.064

Chapter 6

Conclusions and Future Prospects

Polyacrylamide/carboxymethyl guar gum polymeric hydrogel-based metal ion sensor was successfully synthesized by in situ incorporation of *meta*-benziporphodimethene using water as a solvent. Since *meta*-BPDM is hydrophobic in nature for dissolving this, a mixture of acetone and water was used. This hydrogel successfully sensed Zn^{2+}, Cd^{2+} and Hg^{2+} individually and in mixture by showing colour change from red to bluish-green. The synthesized sensor recognizes Hg^{2+} metal ions up to 0.5 mg/L, which is quite comparable to the above permissible limit. Furthermore, it has also been observed that the sensing time decreases with the increase in temperature. This is the first report on polymeric hydrogel that can be used for sensing zinc, mercury, cadmium metal ions in an aqueous medium. Since the monitoring of heavy metal contamination in wastewater is an important step in ensuring human and environmental health. Excess levels of heavy metal may be responsible for several short-term and long term health effects. m-BPDM embedded PAM/CMG polymeric hydrogel-based metal ion sensor was successfully explored for monitoring zinc ions in E. coli bacterial cells and Zn^{2+}, Cd^{2+} and Hg^{2+} in the effluent from the industry with high sensitivity and selectivity. The colour change was visually detected. This probe is a cost-effective and environmentally friendly on-site real-time colorimetric sensor of Zn^{2+}, Cd^{2+} and Hg^{2+} in the aqueous medium. The sensor provides indicator free detection and opens the possibility for solid-state biosensors specific to Zn^{2+}, Cd^{2+} and Hg^{2+}.

The porous structure of modified copolymer-based hydrogel was beneficial for permeation of metal ions into it. The optimum pH was found to be 6.5 and Zn^{2+}, Cd^{2+} and Hg^{2+} achieved adsorption equilibrium within 12 h. The order of adsorption in the multicomponent system was found to be $Hg^{2+} > Zn^{2+} > Cd^{2+}$. The adsorption data fit very well to the Langmuir adsorption isotherm model and pseudo second-order equation. It is found that the adsorption of Hg^{2+} is better than Zn^{2+} and Cd^{2+} under similar conditions due to difference in affinity or binding constants sequence $Hg^{2+} > Zn^{2+} > Cd^{2+}$ with the incorporated *meta*-BPDM in the PAM/CMG hydrogel. The obtained result establishes a suitable method with promising applications for efficient removal of Zn^{2+}, Cd^{2+} and Hg^{2+} from their aqueous solutions.

Future Work

- The sensor provides indicator free detection and opens the possibility for solid-state biosensors specific to Zn^{2+}, Cd^{2+} and Hg^{2+} .
- Designing new formulations of *meta*-BPDM embedded hydrogels based on biodegradable polymers such as raw wool , carboxymethyl tamarind etc. and exploring their real-time applications in sensing and removal of Zn^{2+}, Cd^{2+} and Hg^{2+} from biological and environmental samples.
- This *meta*-BPDM embedded PAM/CMG polymeric hydrogel can be applied in the field of the quantification and removal of Zn^{2+}, Cd^{2+} and Hg^{2+} from the industrial effluent or real wastewater.

List of Publications

- Deepti Chauhan, Anil Kumar, Sudhir G. Warkar., Synthesis, characterization and metal ions sensing applications of *meta*-benziporphodimethene embedded polyacrylamide/carboxymethyl guargum polymeric hydrogels in water. Environmental Technology, 43:7, 2022 , 991-1002, https://doi.Org/10.1080/09593330.2020.1812730.

- Deepti Chauhan, Anil Kumar, Sudhir G. Warkar., Modified polymeric hydrogels for the detection of Zn^{2+} in E. Coli bacterial cells and Zn^{2+}, Cd^{2+} and Hg^{2+} in industrial effluents, Environmental Technology, May, 2021 https://doi.org/10.1080/09593330.2021.1928294.

- Deepti Chauhan, Anil Kumar, Sudhir G. Warkar., An efficient adsorbent for the removal of Zn^{2+}, Cd^{2+} and Hg^{2+} from the real industrial effluents. International Journal of Environmental Science and Technology IJEST, 19, 2021, 1483-1494 https://doi.Org/10.1007/s13762-021-03615-5 .

Conference proceedings

- Worked as organizing team member in the TEQIP-III sponsored one week faculty development program on "polymer analysis and application: Current scenario during 4-8 June 2018 organized by Department of Applied Chemistry, Delhi Technological University, Delhi.

- Presented a research paper titled hydrogel: metal ion sensor at 3rd international conference on advanced production and industrial engineering (ICAPIE 18) organised by centre for advanced production and industrial engineering research (CAPIER), Delhi Technological University, Delhi, India during October 5-6, 2018.
- Participated at the international conference on researches in science and technology (ICRST-19) held on 02 march 2019 at Jaipur Rajasthan.
- Participated in Online Training/Lecture on the topic Prospects of Nano-materials Modified Conducting Paper-Based Biosensors for Cancer Detection by Prof. B.D. Malhotra, on 12th June 2020 Delhi Technological University, Delhi.
- E-poster presentation in the International Virtual Conference on 'Recent Advance in Organic Medicinal and Biological Chemistry' RAOMBC-2020, organized by the Division of Chemistry, School of Advanced Sciences, Vellore Institute of Technology, Chennai during 8th & 9thJuly 2020.
- Participated in the International Virtual Conference on 'Innovations in Chemical Sciences-2020: An International Meet for Quality and Quantity (ICSIMQQ-2020)', organized by the Division of Chemistry, School of Advanced Sciences, Vellore Institute of Technology, Chennai during 21st & 22nd August 2020.
- Participated in Virtual Conference on 'Recent Advances in Bis and Tetra-Pyrrolic Molecular Materials' organized by Department of Chemistry, Central University of Kerala during 24-26th August, 2020
- Participated in International Summit on Quality Indices in Higher Education - 2020, held during 6th to 7th November, 2020 at Delhi Technological University, Delhi.
- Participated in faculty development program on plastic recycling challenges and opportunities from 15 to 19 February 2021 Central Institute of Petrochemicals

Engineering and Technology IPT Lucknow, Department of Chemicals and Petrochemicals Ministry of Chemicals and Fertilizers Govt. of India.

- Participated in One-Day virtual Workshop on “Accelerators/Incubation-Opportunities for Students & Faculties – Early-Stage Entrepreneurs”, recommended by the Institute Innovation Council (IIC) of DTU as per mandate of Innovation Cell, Ministry of Education (MoE) GOI, organized by Department of Applied Chemistry, Delhi Technological University on Saturday, 19th June, 2021.