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# Synthesis of a Novel Raw Wool and Polyacrylamide-Based Hydrogel as a Colorimetric Sensor

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**Abstract:** We have developed a robust method for the detection of heavy metal ions zinc, cadmium, and mercury in water. In this study we have synthesized a hydrogel based on biopolymer that is raw wool obtained from eszvMarino sheep and used this hydrogel as heavy metal ion sensor in the water. We have incorporated meta- benziporphodimethene ligand in-situ in the hydrogel synthesis, which shows selectively color-changing characteristics when immersed in Zn<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>2+</sup> metal ions aqueous solution. This hydrogel shows selective response towards Zn<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>2+</sup> metal ions in a competitive environment. Meta-BPDM was responsible for the selectivity of hydrogel towards Zn<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>2+</sup> metal ions in water. This selective sensing behavior of raw wool based hydrogel has given a novel existence to our study. The synthesized hydrogel was studied for sensing applications and characterized by using FTIR, TGA, and SEM techniques.

Keywords: Hydrogel, Colorimetric Sensor, Heavy Metal, meta-Benziporphodimethene.

## 1. Introduction

Environmental contamination by heavy metal ions is a real and growing problem that urgently needs to be monitored. Heavy metals have high atomic weights and densities initially known heavy metals are thallium, gallium, and hafnium. Heavy metals are essential nutrients in small amounts but are toxic in large quantities. They are non-biodegradable, toxic and are responsible for the contamination of the natural resources in the environment including water. Some of the heavy metals are hazardous even at trace levels such as Arsenic, Lead, Cadmium, Mercury, and Chromium. They are considered to be highly harmful and toxic to human health. This results to the requirement of efficient, easy and accurate techniques for the detection of heavy metal ions in water. Heavy metals are commonly released in wastewaters by various industries such as chemical manufacturing, mining, paint, coating, extractive metallurgy, and nuclear power plants. Polymers containing one or more electron donor atoms like O, N, P and S that can easily form coordinate bonds and chelation with metal are known as poly-chelatogens. Polymeric hydrogels having hydroxyl, amide, amine, ammonium, and carboxylic acid groups can bind with heavy metal ions and act as a good poly-chelatogens. Therefore, they can be used for water purification applications. For instance, Acrylamide and its N- substituted derivatives based polymeric hydrogels are widely used for the applications in various fields<sup>1)</sup>. Zinc is

essential for human beings, animals, and plants but excess consumption can cause severe health effects. Heavy metals ions are bio accumulative, non-biodegradable, and emit toxic pollutants in the environment. Mercury and cadmium metal ions are becoming increasingly crucial for determination due their toxicity in the environment. Their contamination can lead to various health issues, like kidney toxicity, paralysis, physiological metabolic disorders, birth and genetic defects. Mercury inorganic salts can even be corrosive to our eyes and skin. It gets very easily absorbed by the body of human beings and its discharge occurs at a very slow rate<sup>2, 3, 4)</sup>.

Cadmium is a soft and silvery white metal that is chemically similar to zinc and mercury due to filled d-orbital. They are spectroscopically silent metal ions hence their detection in water is difficult. Cadmium metal is widely used in batteries, pigments, corrosion resistant steel plating, plastics stabilizers and solar panels. It can cause acute and chronic disease. It can cause bone mineralization, fragile bones, kidney intoxication and damage our heart. Zinc has numerous applications in our industry such as in galvanization of iron, cathode in batteries, pharmaceuticals, pigments and as catalysts. Small amounts of zinc do not have considerable effects on human body but large quantities can cause damage to pancreas, and arteriosclerosis<sup>5)</sup>.

A hydrogel firstly appeared in 1894, is a 3-Dimensional, cross-linked polymer solid prepared from physical and chemical crosslinking. These soft and wet materials can

be made into smart materials by chemical modifications<sup>1)</sup>. These are the polymeric network formed by hydrophilic polymer chains. The hydrophilicity provides ease in the absorption of big quantities of water, which causes the gel to swell and maintain its 3-D structure<sup>6)</sup>. Swelling behaviour depends on the pH, temperature and ionic strength of the solution. A hydrogel can even contain more than 90% water<sup>1)</sup>. Hydrogel emit various properties like mechanical flexibility, opacity, porosity, etc.

Acrylamide is an organic compound, its chemical formula  $\text{CH}_2=\text{CHC}(\text{O})\text{NH}_2$ . Acrylamide is an odourless white crystalline solid, soluble in water<sup>7)</sup>. It is also soluble in various other organic solvents. Acrylamide is stable at room temperature. Under UV light or at its melting point, acrylamide can violently polymerize. Acrylamide monomers can easily copolymerize by free radical mechanism under mild conditions with various functional groups which are ionizable, reactive, thermosensitive etc.<sup>8)</sup>. Wool is made from natural fibres; it is a fibrous covering from sheep. It is a protein fibre, primarily made of keratin-based proteins which contributes in its high elasticity. This fibre is the earliest known, can be spun and woven by various methods into cloth. Production of wool has declined over the years, highly used in 1990, but now it is fairly stable<sup>9)</sup>. Raw wool constitutes of some contaminants. These also depends on the breed, environment, nutrition etc. Some animals producing wool fibres are Merino, Angora, Cashmere, Mohair, Yak, Camel, etc. The quality of wool fibre is based on its breeding conditions, food, weather conditions and general care. Protein chains are contained within the twisted molecular chain. The protein chains are coiled in a helical shape like a spring. It is a stiff structure due to the presence of hydrogen and disulphide bonds. Each helix is coiled together for stiffening. The coil provides the wool with the desired flexibility and resilience<sup>10)</sup>. The surface morphology is shown in Fig. 1.

Colorimetric sensors have gained wide popularity in recent years. Colorimetry is a scientific technique, sensors belonging to the optical sensors. This technique is used to determine the concentration of coloured compounds<sup>11)</sup>. Sensors change colour when regulated by an external stimulus. This technique is the application of Beer-Lambert law, pronouncing that the concentration of a solute is proportional to the absorbance and the length of light path through the solution<sup>12)</sup>. In comparison to fluorescent sensors, this offers some obvious advantages. Colorimetric sensors have low cost, high accessibility, ease of usage. These have gained popularity over the years due to sensitive and selective response towards various analytes. Numerous methods have been deployed to detect metal ions typically, the systems used to detect metal ions require high-efficiency liquid chromatography, atomic absorption spectrometry (AAS), ICP-MS, and fluorescent sensors have been used for the detection of metal ions. These are used because of their simplicity and ease in operation<sup>6, 2)</sup> but there are many limitations have been

faced while using these techniques. For instance, fluorescent probes are associated with background fluorescence and are relatively dispersed in the entire solution which affects the sensitivity for detection<sup>1)</sup>. It is difficult to separate a fluorescent probe from a solution which limits its reuse, AAS and ICP-MS techniques are expensive and require highly trained personnel<sup>3)</sup> Although, such methods can pose ultrasensitive analytic results. These require expensive types of equipment, complicated and time taking experiments.

To overcome this, we have devoted our effort towards obtaining elementary and inexpensive methods that allow us to visual detection of heavy metal ions in water. In this study, we have employed a new strategy for designing sensors for  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$  metal ions in water. We have used acrylamide to improve extraction capacity and N, N'-methylenebisacrylamide (MBA) was used as a cross-linker. We have obtained raw wool from Merino sheep. Heavy metals are harmful and toxic, so we have focused on a selective and sensitive method. Our method is easy to operate and helps in viable and simple visual detection.

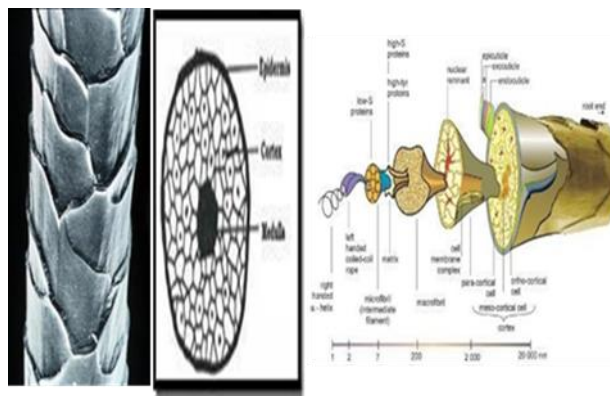


Fig.1: Microscopic appearance of wool<sup>13-14)</sup>.

## 2. Experimental Section

### 2.1 Chemical Used

Sodium hydroxide (NaOH), Hydrochloric acid (HCl), Acrylamide, Potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ), Acetone and N, N'-methylenebisacrylamide. They are obtained from SRL and used as supplied. Raw wool obtained from merino sheep. Meta-Benzporphodimethene was synthesized in lab according to our previous reports<sup>15-20)</sup>. Deionized water was used for sample preparations.

### 2.1 Instrumentation

Magnetic Stirrer, pH meter, weighing balance, The Fourier-transform infrared spectrophotometer (NICOLET 380 FTIR), Thermogravimetric analysis (Perkin Elmer TGA 4000), Scanning electron microscopy (JEOLJSM-6610LV).

### 2.3 Synthesis

**Preparation of Wool solution:** 0.625 molar solution of

NaOH was prepared and mixed with 1.5 gm. of raw wool using a magnetic stirrer under boiling temperature at 200 rpm. Cooled the solution for 30 min and maintained neutral pH using HCl. Added distilled water to increase solution volume to 100 ml.

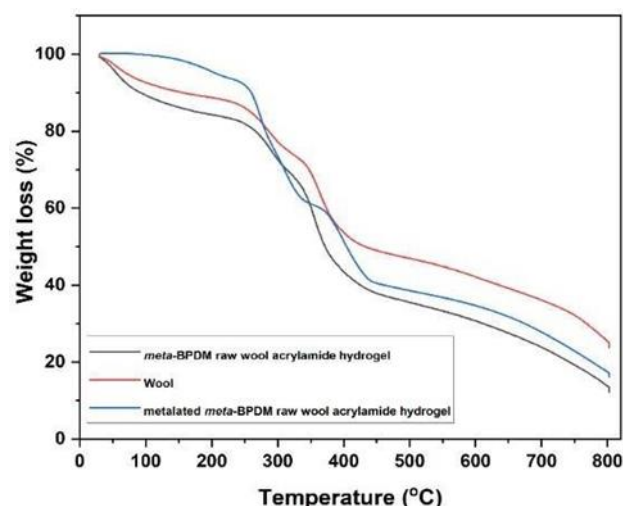
**Preparation of hydrogel:** 1gm of Acrylamide was dissolved in 10 mL of distilled water and 5ml of fresh wool dissolution added into the acrylamide solution. Fresh meta-BPDM was dissolved in 2mL of acetone which was then added to the first solution. After 15 min 1gm of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> initiator added gently and mixed for next 30 min and then added 0.03gm of MBA crosslinker and mixed it well for 40 min. Poured the reaction mixture into a test tube and kept at 75 °C for 1 h, 30 minutes underwater bath for the solidifying process. The obtained hydrogel was washed using deionized water to remove unreacted chemicals and cut into slices, dried at room temperature first and then in oven for overnight

### 3. Result and Discussion

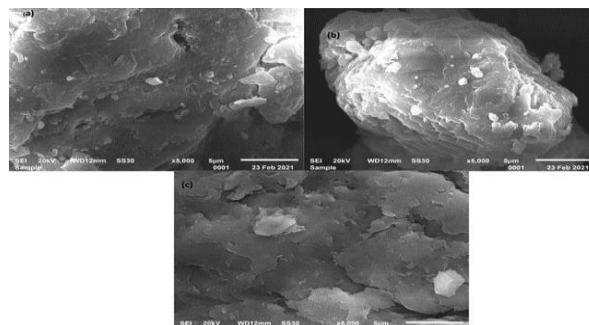
#### 3.1 Characterization

**Thermo gravimetric Analysis (TGA):** This is a technique by which thermal stability of a material is determined by monitoring the materials mass with the change in temperature. This can be done in different atmospheres like air, vacuum, inert gas, etc. This data is then represented on a graph with percentage of initial mass on Y-axis and time or temperature on X-axis. This plot is called the TGA curve. The TGA curve appears as steps with horizontal and curved points. It can be used to determine the composition of material, kinetics of reaction in fields of pharmaceuticals, food, polymer applications. Fig.2 shows TGA curves plotted with temperature against percentage weight loss in nitrogen environment. By using TGA curves we determined thermal stability of our polymeric materials and observed the weight change starting from 40 °C to 800 °C. Finally, the sample has been degraded and turned to ash. TGA for meta- BPDM raw wool polyacrylamide hydrogel shows that initial loss of weight of about 10% around 40 to 100 °C is due to loss of water in form of vapors and other components which are attached to sample surface physically. The second stage of weight loss at about 250 °C shows the degradation of wool fiber, the amide group, breaking of hydrogen and sulfide bonds. The final decomposition was observed above 400 °C due to the degradation of polymeric backbone and the structure starts losing its strength. The TGA curve of metalated m-BPDM raw wool acrylamide hydrogel shows that slow loss in the weight starts from 100°C and continues till 220°C due to detachment of physically attached components and vaporization. The main stage of weight loss starting from 270°C to around 320°C and around 25-30% weight is lost, leaving ~60% of material. Degradation from 375°C to 430°C is result of breaking of crosslinking. The decomposition of material starts above

500°C due to degradation of organic backbone of hydrogel. The results obtained from thermo gravimetric analysis of wool shows that the initial weight loss between 50 to 100 °C is due to the vaporization of water and some components that are physically attached to the sample. The second stage of weight loss starts at about 270 °C due to degradation of the wool fiber, hydroxyl, and amide group's starts. Degradation from 350 to 400°C was due to breaking of sulfide linkage, crosslinking. Final decomposition above 500 °C was due to organic backbone degradation of hydrogel,



**Scanning electron microscopy (SEM):** This is used in studying the surface of material with the help of a focused electron beam. This high energy electron beam creates various signals on interaction with various atoms and helps in understanding surface topography and composition of material. Fig. 3. Showing surface morphology of raw wool- acrylamide hydrogel is rough, porous and uneven which is remains unaffected by embedded meta- BPDM However, metalation make the morphology more connected and compact due to complexation with metal ions.



**Fig.3:** Showing surface morphology of (a) Raw wool-acrylamide hydrogel (b) meta-BPDM raw wool-acrylamide hydrogel and (c) metalated meta-BPDM raw wool-acrylamide hydrogel.

**Fourier Transform Infrared spectroscopy (FTIR):** FTIR spectra of metalated meta-BPDM raw wool

acrylamide hydrogel showing the broad peak around 3450 cm<sup>-1</sup> is characterization of OH stretch and the peak observed at 3300 cm<sup>-1</sup> is due to presence of amide group i.e., CONH<sub>2</sub>. The sharp peak due to carbonyl group is observed at ~1690 cm<sup>-1</sup> and in the fingerprint region the small peak at ~1450 cm<sup>-1</sup> is due to OH bending. The C-H bending peak is observed at ~1380 cm<sup>-1</sup>. No peak is observed around 2000-2500 cm<sup>-1</sup> indicates that no triple bonded C is present in the structure. In meta-BPDM raw wool acrylamide hydrogel FTIR spectra the broad peak at around 3430 cm<sup>-1</sup> is the characteristic peak of hydroxyl group stretch. Peak adjacent to the OH is due to amide group which is observed with the help of peak around 3310 cm<sup>-1</sup>. The sharp and clear peak at 1690 cm<sup>-1</sup> shows the presence of C=O stretching. The dual peaks around 1400 cm<sup>-1</sup> are again for hydroxyl group but this time for OH bend. Small peak around 1370 cm<sup>-1</sup> is characterisation of vinylidene C-H bending. Another peak in the finger print region at ~1150 cm<sup>-1</sup> could be for C-H bond. For raw wool acrylamide hydrogel, the peak observed at ~3400 cm<sup>-1</sup> shows characteristics of stretching vibration of hydroxyl group (OH). The peak ~3300 cm<sup>-1</sup> is related to the amide group (CONH<sub>2</sub>). The clear peak around 1700 cm<sup>-1</sup> shows characteristics of the carbonyl group present in acrylamide, wool and hydrogel. The small peak at around 1400 cm<sup>-1</sup> shows characteristics of -OH bending.

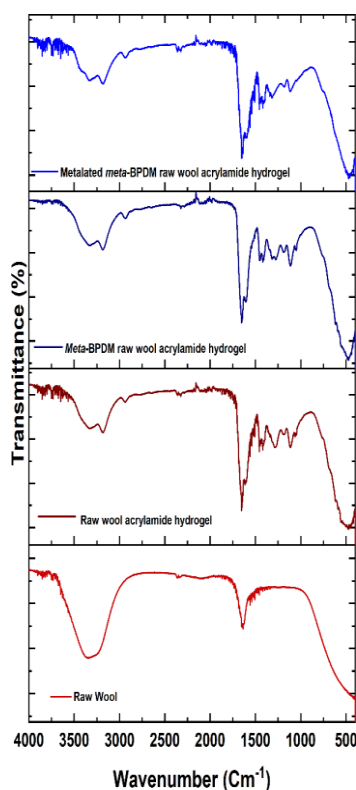


Fig.4: Showing FTIR spectra.

The disturbance peaks around ~1350 is due to Vinylidene C-H in- plane bending. Metalated meta-BPDM raw wool acrylamide hydrogel and meta-BPDM

raw wool acrylamide hydrogel shows identical spectra with raw wool-acrylamide hydrogel. Which indicates that the insertion of this ligand does not affect the IR spectra of hydrogel. The ATR-FTIR spectrum of the wool fibre solution showing peaks between 3300 and 3500 cm<sup>-1</sup> is due to the presence of an amide group O-H stretching. The peak observed at 3278 cm<sup>-1</sup> shows characterization of N-H group present in wool chemical structure as shown in Fig. 1. The clear peak at 1680 cm<sup>-1</sup> shows the presence of carbonyl group (C=O) stretching in the structure<sup>20-25</sup>.

**Sensing Application of Synthesized Hydrogel:** The sensing behavior of the synthesized polymeric hydrogel was performed in aqueous solutions of metal ions. It was found that the hydrogel changes its colour only with Zn<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>2+</sup> in the presence of other alkali, alkaline metal ions aqueous solutions. The meta-BPDM organic ligand a red- coloured molecule is responsible for this selective nature. This was incorporated in situ in hydrogel synthesis. The hydrogel changes its colour upon metalation from red to dark blue. The binding constant of these metal ions with the meta-BPDM present in polymeric network is responsible for selectivity in sensing. The hydrogel was allowed to disperse in aqueous metal ion solution and observed the colour change in them with time at room temperature. The sensitivity of the polymeric hydrogel was found to be 1, 1.5, and 4 mg/L with Hg<sup>2+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup> in 1.5 h, 2 h and 4 h respectively at 60 °C. Minimum time and high sensitivity were shown by mercury metal ions detection followed by zinc and cadmium respectively. This can be explained by the kind of interaction occurring between metal ions and meta-BPDM.<sup>25-32</sup>.



Fig.5: Showing color change property of hydrogel.

#### 4. Conclusion

In a nutshell, a novel meta-benziporphodimethene incorporated raw wool- polyacrylamide based polymeric hydrogel was synthesized via free radical mechanism successfully using water as a solvent. Thermogravimetric analysis has shown that this hydrogel has adequate thermal stability and was potentially applied for the sensing of Zn<sup>2+</sup>, Cd<sup>2+</sup> and Hg<sup>2+</sup> in aqueous metal ion solution. This is the first report on raw wool- polyacrylamide based polymeric hydrogel used for sensing zinc, cadmium and mercury metal ions in water. The hydrogel changes its color from red to dark blue which is visually detected hence, showing easy to use. The



minimum detectable concentration of metal ions by the polymeric hydrogel was found to be 1, 1.5, and 4 ppm with  $\text{Hg}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  in 1.5 h, 2 h and 4 h respectively at 60 °C. Further this application can be explored for real time sensing of these metal ions in industrial wastewater. Potential application of this hydrogel can be explored in heavy metal ions removal from the real wastewater. Removal of heavy metal ions from wastewater using this hydrogel is the current focus of our lab.

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