



Development of Modified Pencil Graphite Electrode Sensors by Using Polyaniline and Polypyrrole Based Poly(acrylamide-co-amps) Hydrogels for the Detection of Methylene Blue

RAMESH SELVARAJ^{1*}, SELVANATHAN GANESAN¹
and ELANCHEZHIAN BALACHANDRAVINAYAGAM¹

¹Department of Chemistry, AVC College (Autonomous), Mannampandal, Mayiladuthurai-609 305
(Affiliated to Bharathidasan University, Tiruchirappalli), Tamil Nadu, India.

*Corresponding author E-mail: rameshthss@gmail.com

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ABSTRACT

The present study is to synthesize hydrogels based on acrylamide, 2-acrylamido-2-methylpropane sulfonic acid and copolymers of acrylamide/2-acrylamido-2-methyl-1-propane sulfonic acid with aniline and pyrrole to detect methylene blue dye. The copolymers samples composed of acrylamide with different amounts of 2-acrylamido-2-methylpropane sulfonic acid, aniline and pyrrole were synthesized using the cross linker N, N'-methylene bis acrylamide and the initiator potassium per sulfate by a free radical polymerization method. The cheap and disposable Pencil Graphite Electrodes using pencil leads, were developed by surface modification with polymeric hydrogels coating and were considered as working electrodes and sensors. Cyclic Voltammetry, Differential pulse Voltammetry and Square Wave Voltammetry was used to study the sensing property of the electrodes. The molecular structure of the hydrogel polymers was characterized by means of Fourier Transform Infrared Spectroscopy. The morphology of the resulting hydrogels polymers was studied by Scanning Electron Microscopy and X-ray Diffraction. The sensing properties of the polymeric hydrogels coated electrodes were tested in different concentration of Methylene Blue solution with variable dipping time of the electrodes. The Cyclic Voltammetry characterization proved that the copolymerization of aniline and pyrrole with the hydrogels and the hydrogels coated Pencil Graphite Electrodes as a sensor led to a considerable improvement in sensing behavior towards the methylene blue dye by producing significant current response.

Keywords: Copolymers, Hydrogels, Pencil graphite electrodes, Methylene blue, Cyclic voltammetry.

INTRODUCTION

Hydrogels are cross linked three dimensional polymer network systems synthesized via polymerization of monomers which are hydrophilic in nature with the cross linker. The

applications of the superabsorbent polymers are employed in super capacitors, conducting materials and in sensors. The hydrogels synthesized by using conducting polymers have shown significant advantages in various aspects. The conducting polymer based hydrogels have an extensive



applications in chemical separations, drug delivery and controlled release in agriculture. Only a few studies have been reported on the synthesis of super absorbent polymers with the conducting polymers and inorganic materials. The effect of monomer concentration, amount of cross linker and initiator and conducting materials like aniline, pyrrole, graphite, copper, etc., on the conductivity of hydrogels synthesized are also investigated. The versatility of the hydrogels has various applications as conducting materials, sensors, drug release materials and biomaterials¹.

Sensors in electrochemical analysis have been developed and successfully applied in different areas in the last few decades. Substantial efforts have been made in the development of portable electrochemical sensors to investigate organic and inorganic environmental pollutants²⁻⁵. The electrodes were often prepared with suitable modifier materials to achieve improvements in selectivity and sensitivity⁶⁻⁹. The development of the newer electrode modifier material is a progressive effort to fulfill the demands of modern electrochemical technology. Application of surface modified carbon electrode with nanomaterials in environmental pollutant monitoring is a promising electrochemical sensing technique. Because of their higher sensitivity, good conducting property with smaller residual current and durable nature, the electrochemical sensors exhibit their performance in different fields. Carbon paste electrodes demonstrate their extensive applications since the introduction by Adams in 1958¹⁰⁻¹³.

The Glassy Carbon, Carbon paste, Carbon filler, Screen printed carbon strips, etc., are the most frequently used electrodes as electrochemical sensors. Apart from the carbon based electrodes, some commonly known materials are also used for the preparation of the novel electrodes for various electrochemical sensing^{14,15}. Now a days, a huge variety of nanomaterials have been synthesized and their applications in electrochemical sensor development show immense progress. The utilization of unique and distinct characteristics of nanomaterials by modern electroanalytical methods is an emerging field on the characterization of electroactive species.

Nevertheless, the main issue of conventional carbon based electrode is fouling of their surface during the electrochemical determinations. The intermediate products formed by the electrochemical reactions on the electrode surface essentially cleaned prior to each measurement for good results. In order to resolve these issues of the conventional glassy carbon based sensors, various surface modifications have been developed like metallization, derivatization and doping¹⁶⁻¹⁸. Some cost effective disposable electrodes such as screen printed electrodes and the pencil graphite electrodes have been used to overcome such difficulties. The pencil graphite electrodes have more advantages over the screen printed electrodes due to their good mechanical strength, easy availability and low cost. The development of pencil graphite electrode based electrochemical sensors is a significant one to overcome the drawbacks of the conventional GC based sensors. Now a days demand of low cost, easy to fabricate onsite voltammetric sensors are progressively increasing.

The sensitivity and selectivity of pencil graphite electrodes can be enhanced by the surface modification with nanomaterials, conducting polymers or by a combination of both. Different methods are available to modify the surface characteristics of the electrodes. This is achieved with one or more modifier compounds over the electrode surface by coating, casting or dispersion to combine the chemical, electrochemical and catalytic properties of the modifier.

In the present study a novel hydrogels based on Poly(acrylamide/AMPS), Poly(acrylamide/AMPS)/ polyaniline and Poly(acrylamide/AMPS)/polypyrrole synthesized via free radical copolymerization using the cross linker methylene bisacrylamide and the initiator potassium per sulfate. The synthesized hydrogels were coated on the Pencil Graphite Electrodes which were used as sensors for the determination of methylene blue dye. Detailed characterization study was performed by Cyclic Voltammetry, Square Wave Voltammetry, Differential pulse voltammetry, Fourier Transform Infrared Spectroscopy, X-ray Diffraction and Scanning Electron Microscopic techniques.

EXPERIMENTAL

Materials

Acrylamide, 2-acrylamido-2-methylpropanesulfonic acid (Merck) was used as purchased. Potassium persulfate (KPS) as an initiator and N,N'-methylene bisacrylamide (MBA) as a cross linker, aniline, pyrrole and methanol were purchased from Sigma Aldrich. Aniline and pyrrole monomer were distilled prior to use. All the reagents were analytical grade and used directly without further purification. Pencil leads (0.7mm, Kokuyo Camlin Ltd, India) were purchased from a stationary shop. Deionised water was used in the preparation of hydrogels.

Synthesis of Poly(acrylamide/AMPS) polymer

Polymerization reaction was carried out in 1:2 methanol/water solvent mixture at 60°C in nitrogen atmosphere and in the presence of KPS as initiator and MBA as a cross linker. Aqueous solution containing AM (0.5 g), AMPS (0.5 g, 0.3 g, 0.1 g), MBA (0.05 g) and KPS (0.05 g) were prepared using methanol water mixture. The contents were placed in a polymerization tube and nitrogen gas was purged for 15 minutes. Polymerization reaction was controlled in a thermostatic water bath at 60°C along with constant stirring by a magnetic stirrer for 3 hours. The gelatinous polymer mass thus obtained was used for further studies.

Preparation of Poly(acrylamide/AMPS)/PANI and Poly(acrylamide/AMPS)/PPYR hydrogels

The freshly prepared gelatinous Poly(acrylamide/AMPS) hydrogels were taken in two sets of polymerization tubes. Aniline and pyrrole monomer concentration was varied as 0.1 mL, 0.3 mL and 0.5 mL and was added to the hydrogels. The mixtures were allowed overnight to disperse aniline and pyrrole monomers uniformly in to the hydrogel polymer matrix at room temperature. A dark green colored Poly(acrylamide/AMPS)/polyaniline and black colored poly(acrylamide/AMPS)/polypyrrole hydrogel polymer resulted was used for electrode preparations.

Preparation of Poly(acrylamide/AMPS)/PANI and Poly(acrylamide/AMPS)/PPYR hydrogels coated Pencil Graphite Electrode Sensor

The Poly(acrylamide/AMPS)/PANI and Poly(acrylamide/AMPS)/PPYR hydrogel was taken in the separate polymerization tubes. Pencil leads were dipped into 1 cm height in the hydrogel matrices for 24 hours. The polymer

coated pencil leads were taken outside and dried at room temperature. Poly(acrylamide/AMPS)/PANI and Poly(acrylamide/AMPS)/PPYR coated Pencil Graphite Electrodes were used to study the electrochemical response of MB dye in aqueous medium.

Methylene blue absorption

A stock solution of 400ppm MB dye was prepared with deionized water. 40, 120 and 200ppm of MB working solutions was prepared by diluting the stock solution. Then hydrogel coated electrodes (PGEs) were dipped in 5 mL of working solutions and allowed to swell for 10 min, 20 min and 30 min in each concentration of MB solution. The electrodes are washed with water and electrochemical investigations were carried out to study their sensing behavior.

Measurements and Characterization techniques

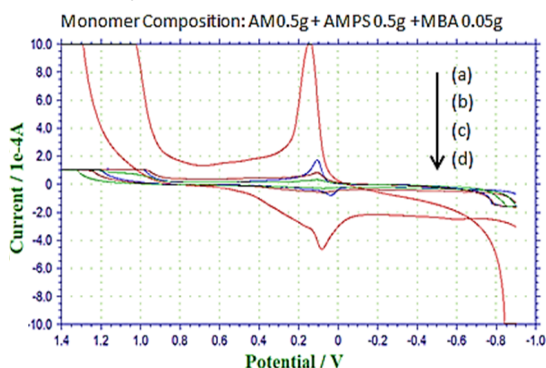
Poly(acrylamide/AMPS), Poly(acrylamide/AMPS)/PANI and Poly(acrylamide/AMPS)/PPYR hydrogels were characterized with PerkinElmer, Spectrum Two FTIR spectrometer using KBr pellets between the wave region of 4000 cm⁻¹ to 400 cm⁻¹. Morphological study of samples was carried out using the Carel Zeiss, Model EVO-18 scanning electron microscope. The X-ray diffraction studies of the hydrogels were carried out using a Bruker D8 Advance X-ray powder diffractometer using CuK α radiation. The electrochemical studies were carried out using a CH Instruments model 620 electrochemical workstation in a single compartment three electrode cell assembly.

RESULTS AND DISCUSSION

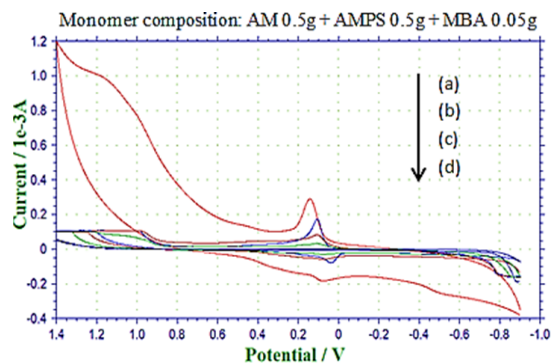
Cyclic voltammetry

Cyclic voltammetry characterization of hydrogel coated PGEs performed using CH620 software. Voltammetric experiments were performed using a single compartment three electrode system using hydrogel coated PGEs as working electrodes. A Pt wire was an auxiliary electrode and KCl saturated calomel electrode as reference electrode in a potential window ranging from 1.4V to -1.0V at a scan rate of 0.05V/s. The bare PGE, plain hydrogel coated PGE and polyaniline, polypyrrole based hydrogel coated PGE were subjected to voltammetric investigations. The electrochemical response was studied in the pH ranging from 1.0 to 13.0 with methylene blue dye as an analyte. MB dye showed a well defined

cyclic voltammogram of the fabricated electrodes with a better current response in pH 1.0 (Fig. 1). Effect of scan rate studies between 0.025V/s and 0.25V/s showed a better response at 0.050V/s was used for further studies. The influence of monomer ratio was studied for plain, polyaniline and polypyrrole based hydrogels. The hydrogels prepared with 0.5 g AM, 0.5 g AMPS, 0.05 g MBA plain and same with 0.1 mL of aniline and with 0.1 mL of pyrrole showed better characteristic response to MB dye. The role of MB dye concentration was also studied from 40ppm to 400ppm. Maximum peak current observed with 200ppm MB solution (Fig. 1,2). The influence of swelling time was studied by allowing the hydrogel coated electrode into a 200ppm MB solution for 10, 20, 30, 40 and 50 minutes. MB absorption reached maximum at 30 min and then there was no significant increase in the peak current. The effect of sensing behavior with different concentration of pyrrole is shown in Fig. 2 and the polymer gel with 0.1 mL pyrrole has more influence than the other concentrations. The Fig. 3 shows the sensing behavior of polymer gel with 0.1 mL of aniline and different concentrations of pyrrole monomer in which polymer gel with aniline monomer has more sensing behavior. Overall CV analysis of the PGEs coated with Poly (acrylamide-co-AMPS)/polyaniline hydrogel showed higher current response than the PGEs coated with Poly(acrylamide-co-AMPS), Poly(acrylamide-co-AMPS)/PPyr and bare electrode.

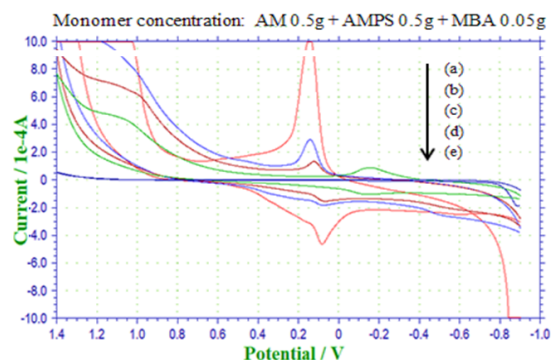


(a) Polymer gel with 0.1 mL of aniline in 200ppm of MB and (b) Polymer gel in 200ppm of MB, (c) Polymer gel in 120ppm of MB, (d) Polymer gel in 40ppm of MB at 30 min swelling time
Fig. 1. Cyclic voltammogram of PGEs coated with Poly (Acrylamide/AMPS)/PANI and Poly(Acrylamide/AMPS) hydrogels at the scan rate of 50mV/s



(a) Polymer gel with 0.1 mL of pyrrole in 200ppm of MB, (b) Polymer gel in 200ppm of MB, (c) Polymer gel in 120ppm of MB (d) Polymer gel in 40ppm of MB and bare electrode at 30 min swelling time

Fig. 2. Cyclic voltammogram of PGEs coated with Poly (acrylamide/AMPS)/PPyr and Poly(acrylamide/AMPS) hydrogels at the scan rate of 50 mV/s

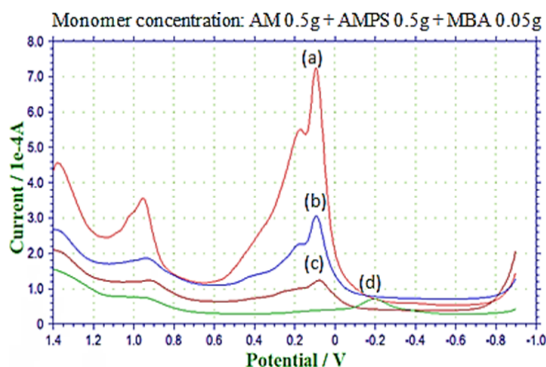


(a) Polymer gel with 0.1 mL of aniline, (b) Polymer gel with 0.1 mL of pyrrole, (c) Polymer gel with 0.3 mL pyrrole (d) Polymer gel with 0.5 mL of pyrrole and (e) bare electrode in 200ppm MB at 30 min swelling time

Fig. 3. Cyclic voltammogram of PGEs coated with Poly(acrylamide/AMPS)/PANI and Poly(acrylamide/AMPS)/PPyr hydrogels at the scan rate of 50 mV/s

DPV and SWV studies

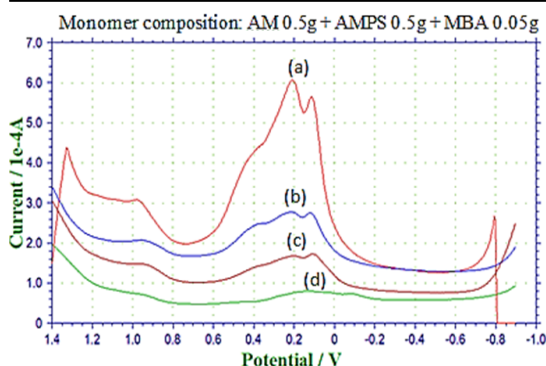
The optimum parameters arrived with CV studies of hydrogel coated PGEs and MB dye concentration was taken for DPV and SWV studies. DPV and SWV experimental parameters were optimized for further studies. The DPV studies reveals that the PGEs hydrogel containing polyaniline has good sensing behavior with a maximum current response of 726.9 μ A than the electrodes coated with polypyrrole Fig. 4. The peak current is shown in Table 1. In the same way PGEs subjected to optimized square wave voltammetric studies. As in the DPV studies, similar type of response was noticed but with a lower peak currents. The 0.1 mL aniline based hydrogel showed a maximum peak current of 609.2 μ A with the electrode dipped with 120ppm of MB dye for a swelling period of 30 minute. Typical square wave voltammogram are illustrated in Figure 5.



(a) Polymer gel with 0.1 mL of aniline, (b) Polymer gel with 0.1 mL of pyrrole, (c) Polymer gel with 0.3 mL pyrrole (d) Polymer gel with 0.5 mL of pyrrole, in 120ppm MB at 30 min swelling time
 Fig. 4. DPV of PGEs coated with Poly(acrylamide/AMPS)/PANI and Poly(acrylamide/AMPS)/PPyr hydrogels at the scan rate of 50 mV/s

Table 1: Voltammetric behavior of PGE coated with Poly(acrylamide/AMPS)/PANI and P(acrylamide/AMPS)/PPyr in 120ppm MB dye: swelling time 30 minute

Plain gel composition	Poly(acrylamide /AMPS)/PANI		Poly(acrylamide /AMPS)/PPyr	
	Aniline (mL)	Peak current (μ A)	Pyrrole (mL)	Peak current (μ A)
0.5 g AM+0.5 g AMPS+0.05 g	0.1	726.9	0.1	311.50
	0.3	300.1	0.3	129.60
	0.5	214.7	0.5	074.67



(a) Polymer gel with 0.1 mL of aniline, (b) Polymer gel with 0.1 mL of pyrrole, (c) Polymer gel with 0.3 mL pyrrole (d) Polymer gel with 0.5 mL of pyrrole, in 120ppm MB at 30 min swelling time
 Fig. 5. SWV of PGEs coated with Poly(acrylamide/AMPS)/PANI and Poly(acrylamide/AMPS)/PPyr hydrogels at the scan rate of 50 mV/s

FTIR analysis of the Hydrogels

The FT spectrum of Poly(acrylamide/AMPS) and Poly(acrylamide/AMPS)/PANI and Poly(acrylamide/AMPS)/PPYR hydrogels were characterized with PerkinElmer, Spectrum Two FTIR spectrometer using KBr pellets between the wave

region of 4000 cm^{-1} to 400 cm^{-1} and are shown in Fig. 6-8. A broad peak corresponding to NH stretching is formed at 3434.08 cm^{-1} . The peak observed at 1645.75 cm^{-1} corresponds to C=O stretching of AM. The peaks around 1110 cm^{-1} , 1045 cm^{-1} and 620 cm^{-1} corresponds to asymmetric stretching of SO_2 , symmetric stretching of the SO_2 and C-S stretching of AMPS respectively. The peak at 2923.53 cm^{-1} is due to CH stretching of polymer backbone. The stretching of C-N band is seen at around 1456 cm^{-1} .

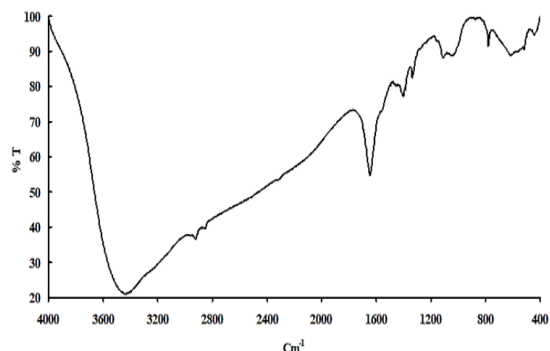


Fig. 6. FTIR Spectra of Poly(acrylamide/AMPS) Hydrogel

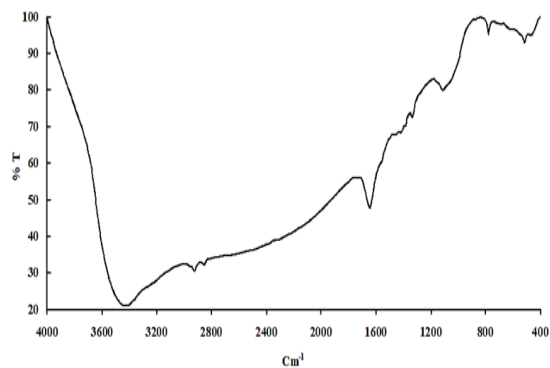


Fig. 7. FTIR Spectra of Poly(acrylamide/AMPS)/PANI Hydrogel

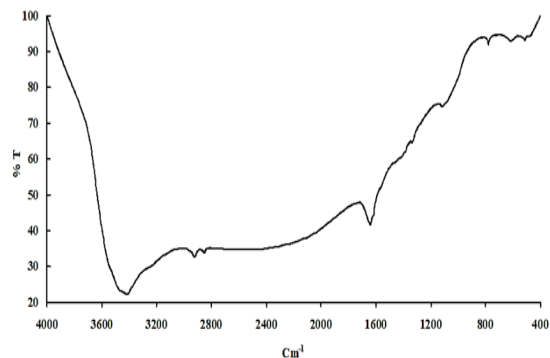


Fig. 8. FTIR Spectra of Poly(acrylamide/AMPS)/PPYR Hydrogel

XRD Analysis

The XRD patterns of the copolymer hydrogels were carried out using a Bruker D8 Advance X-ray powder diffractometer using CuKa

radiation and are shown in Fig. 9-11. 2 θ values range from 10 to 80. The peak pattern of Poly(acrylamide/AMPS), Poly(acrylamide/AMPS)/PANI and Poly(acrylamide/

AMPS)/PPYR is shown in the figures. The XRD analysis showed that the co-polymeric hydrogel materials are more amorphous in nature.

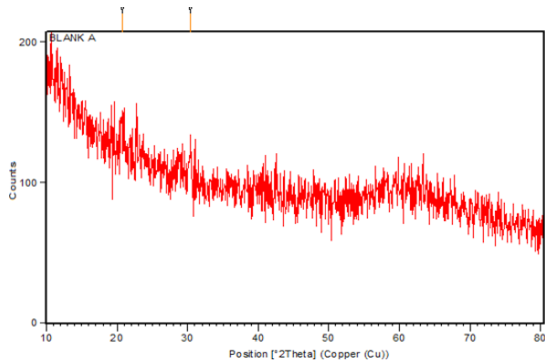


Fig. 9. X-ray Diffraction pattern of Poly(acrylamide/AMPS) hydrogel

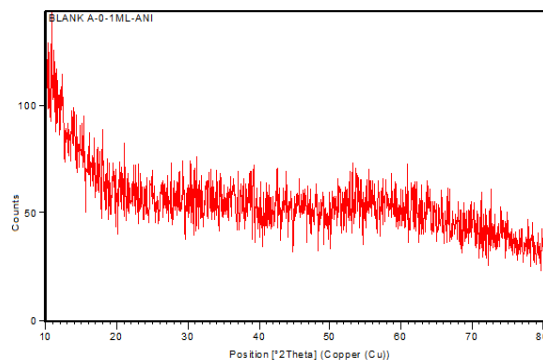


Fig. 10. X-ray Diffraction pattern of Poly(acrylamide/AMPS)/PANI hydrogel

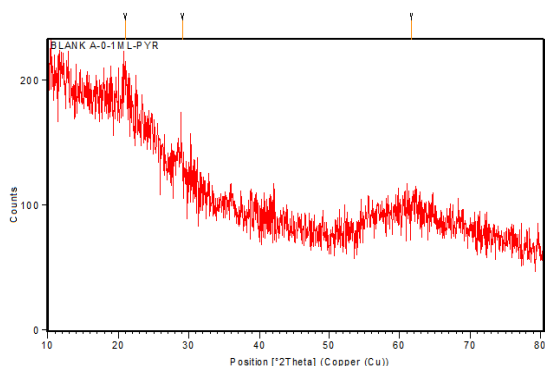


Fig. 11. X-ray Diffraction pattern of Poly(acrylamide/AMPS)/PPYR hydrogel

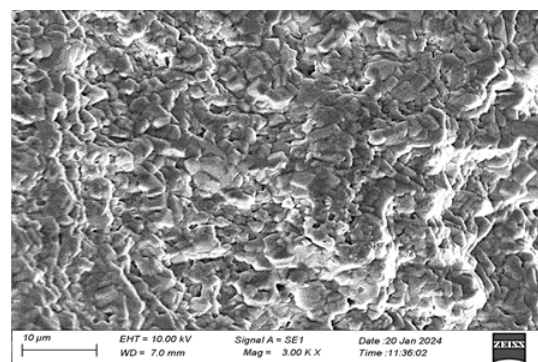


Fig. 12. SEM analysis of Poly(acrylamide/AMPS) hydrogel

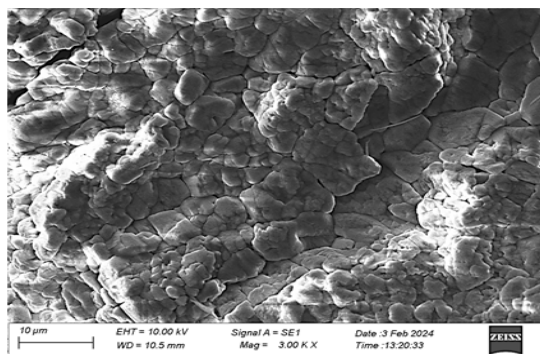
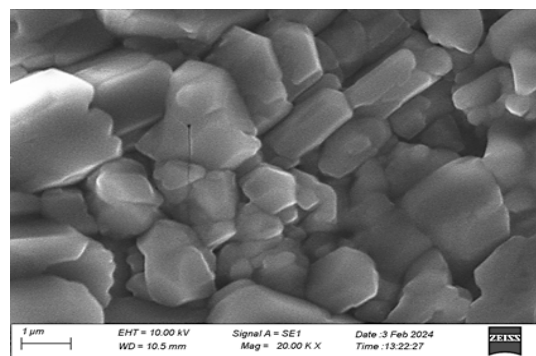


Fig. 13. SEM analysis of Poly(acrylamide/AMPS)/PANI hydrogel



SEM Analysis

The Surface Morphology of copolymer hydrogels was studied by CarlZeiss, Model EVO-18 scanning electron microscope. The SEM images of the hydrogels were shown in Fig. 12-14. The image indicates the presence of copolymers which are uniformly distributed throughout the polymer matrix.

It can be seen from the images that

the Poly(acrylamide/AMPS) hydrogel shows a smooth, less dense and less compact structure. But the Poly(acrylamide/AMPS)/PANI shows a coarse, more dense and highly compact network surface suggesting the connection and formation of polyaniline chain within the Poly(acrylamide/AMPS) polymer matrix. The image of Poly(acrylamide/AMPS)/PPYR shows an irregular, coarse with more porous structure.

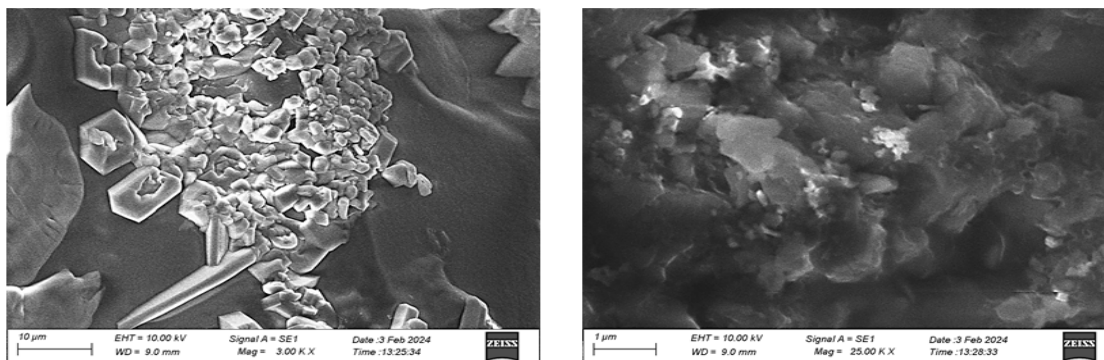


Fig. 14. SEM analysis of Poly(acrylamide/AMPS)/PPYR hydrogel

CONCLUSION

In the present work Poly(acrylamide/AMPS), Poly(acrylamide/AMPS)/PANI and Poly(acrylamide/AMPS)/PPYR hydrogels were synthesized and used for the coating of the pencil leads which are considered as Pencil Graphite Electrodes (PGEs). The polymer hydrogel electrodes were characterized by Cyclic Voltammetry, DPV, SWV, FTIR, XRD and SEM analyses. The electrodes coated with hydrogels prepared with aniline showed higher sensitivity over hydrogel with pyrrole and bare electrodes in the electrochemical response of MB dye under optimum concentration and swelling time. The CV studies revealed that the hydrogels, prepared with polyaniline coated pencil graphite electrodes showed good sensing

efficiency. Due to their excellent sensing behavior, the coated PGEs could thus potentially substitute to the expensive electrodes. Because of the cost effective easy to fabrication, they may be a potential sensor in sensing environmental pollutants.

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Conflict of interests

The authors declare that there is no conflict of interest including any financial, personal or other relationships with other people or organizations that can influence their work.

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