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SYNTHESIS, CHARACTERIZATION AND SENSING BEHAVIOUR OF POLY(ACRYLAMIDE-CO-AMPS) AND POLY(ACRYLAMIDE-CO-AMPS)/POLYANILINE HYDROGELS USING PENCIL GRAPHITE ELECTRODES

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ABSTRACT

The copolymer samples composed of acrylamide with different amounts of 2-acrylamido-2-methylpropane sulfonic acid and aniline were synthesized with a cross-linker N, N'-methylene bisacrylamide and an initiator potassium per sulfate by a free radical copolymerization method. Cheap and disposable pencil graphite electrodes were developed by surface modification with hydrogel polymer coating. The sensing property of the electrodes was characterized by cyclic voltammetry, differential pulse voltammetry, and square wave voltammetry. The molecular structure of the hydrogel polymers was characterized by FT-IR spectroscopy. The morphology of the resulting hydrogels was studied by SEM and X-ray diffraction. The sensing properties of the hydrogel polymer-coated electrodes were tested in different concentrations of methylene blue in deionized water with variable dipping times of the electrodes. The cyclic voltammetric characterizations of a copolymer of aniline with the hydrogels coated pencil graphite electrodes showed higher sensing response to methylene blue dye.

Keywords: Copolymer, Hydrogels, Pencil Graphite Electrode, Methylene Blue, Cyclic Voltammetry.
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INTRODUCTION

Hydrogels have extensive and important applications in chemical separation, drug delivery, and controlled release in agriculture. The unique properties of the hydrogels are their ability to absorb, swell, and retain aqueous solutions equal to a hundred times their own weight.[1-5] The presences of ionic functional groups in hydrogels make them to absorb and to trap ionic dyes such as methylene blue from wastewater. Concerning the hydrolytically stable nature and strong acid functionality, the hydrogels synthesized from acrylamide, 2-acrylamido-2-methylpropane sulfonic acid (AMPS) become more important. The glassy carbon electrode (GCE) has wide applications in electrochemical analysis. But to achieve a high level of sensitivity and selectivity, the GCE is subjected to mechanical polishing, anodization, nanoparticle applications, and deposition with conducting polymers or with polymer nanoparticle composites. But when the electrodes become fouled, one cannot easily discard them due to their highly expensive nature. Electrochemical reproducibility of the GCE surface can only be achieved by a tedious surface polishing procedure and modification process. Therefore it becomes more important to find an alternative for the traditionally used electrodes. The pencil leads are cheap, easily available, easy to dispose of, and have good conducting properties so they are considered to be used as pencil graphite electrodes.[6] The pencil leads are non-polluting and eco-friendly to the environment. These properties draw interest to utilize the pencil leads as an electrode/electrochemical sensor in electrochemical analysis.[7,8] Furthermore, when compared with metallic electrodes like Au or Pt, they provide a large working potential window. According to Bond et al., the background current produced with the pencil graphite electrodes is very small compared to that of GCE and metal electrodes.[9] Nowadays a number of bare and surface-modified pencil graphite electrodes have been developed as sensors.[10] The metals, metal oxide, conducting, and composite polymers have been used for the fabrication of the electrodes. The fabricated electrodes have been used to detect the biologically originated molecules formed from plant materials, serum from human beings, liquid food refreshments, industrial sewages, and various environmental samples.[11,12] The reactive nature, high-level adsorption,

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large potential window, low cost, and simple procedure for modifications make the PGEs good-quality working electrodes. Furthermore one can easily control the surface area of the PGE that undergoes the reaction or sensing behavior based on the analysis. The electrochemical characters of the fabricated electrodes are improved by the nanomaterials which are immobilized in the electrode surface. The nanoparticles can be electrodeposited on the electrode surface which can mediate the electron transfer reaction of electroactive species.[13] This deposition can also be done by simple immersion of the PGEs into the nanoparticle solutions.[14,15] In the present study we aimed to synthesize novel nanocomposite hydrogels based on acrylamide/AMPS and acrylamide/AMPS/aniline via free radical polymerization using the cross-linker methylene bis acrylamide and the initiator potassium persulfate. The synthesized hydrogels were coated on the Pencil Graphite Electrodes which were used as sensors for the determination of methylene blue. Detailed characterization study was performed by Cyclic voltammetry (CV), Differential pulse voltammetry (DPV), Squarewave voltammetry (SWV), FT-IR Spectroscopy (FTIR), X-ray diffraction (XRD) and Scanning Electron Microscope (SEM) techniques.

EXPERIMENTAL

Materials

Acrylamide (AM), and 2-Acrylamido-2-methylpropane sulphonic acid (AMPS) (Merck) were used as purchased. Potassium persulfate (KPS) as an initiator and N, N'-methylene bisacrylamide (MBA) as a cross-linker, Aniline, and Methanol were supplied by Sigma Aldrich. Aniline was 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 used for surface modifications. Deionized water was used in the preparation of hydrogels.

Synthesis of poly(acrylamide-co-AMPS) Polymer

The polymerization reaction was carried out in1:2 methanol/water solvent mixture at 60°C in a nitrogen atmosphere and the presence of KPS as initiator and MBA as a cross-linker. An aqueous solution containing AM (0.5g), AMPS (0.5g,0.3g,0.1g), MBA (0.05g), and KPS (0.05g) was prepared using a methanol-water mixture. The contents were placed in a polymerization tube and nitrogen gas was purged for 15 minutes. The 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-co-AMPS)/polyaniline Hydrogels

The freshly prepared poly(AM-co-AMPS) hydrogels were taken in the polymerization tubes. Aniline monomer concentration was varied as 0.1ml, 0.3ml, and 0.5 ml and was added to the hydrogel. The mixture was allowed overnight to disperse aniline monomer uniformly into the hydrogel polymer matrix at room temperature. A dark green colored poly(acrylamide-co-AMPS)/polyaniline hydrogel polymer was used for electrode preparations.

Preparation of poly(acrylamide-co-AMPS)/Polyaniline Coated Pencil Graphite Electrodes

The poly(acrylamide-co-AMPS)/polyaniline hydrogel is taken in the polymerization tube. Pencil leads were dipped into 1cm height in the hydrogel matrix for 24 hours. The polymer-coated pencil leads were taken outside and dried at room temperature. Poly(acrylamide-co-AMPS)/polyaniline-coated PGEs were used to study the electrochemical response of MB dye in aqueous medium.

Methylene Blue Absorption

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

Measurements And Characterization Techniques

Poly(acrylamide-co-AMPS) and poly(acrylamide-co-AMPS)/polyaniline hydrogels were characterized with PerkinElmer, Spectrum Two FT-IR spectrometer using KBr pellets between the wave region of

4000cm^{-1} and 400cm^{-1}. Morphological studies of samples were 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 Cu Ka 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 voltammetric 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 a saturated calomel electrode was a 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-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). The effect of scan rate studies between 0.025 V/s and 0.25V/s showed a better response at 0.050 V/s was used for further studies. The influence of monomer ratio was studied for plain and polyaniline-based hydrogels. The hydrogels prepared with 0.5g AM, 0.5g AMPS + 0.05g MBA plain, and the same with 0.1ml of aniline showed better characteristic response to MB dye. The role of MB dye concentration was also studied from 40 ppm to 400 ppm. Maximum peak current observed with 200ppm MB solution (Fig.-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 minutes and then there was no significant increase in
the peak current. Typical cyclic voltammograms are shown in Fig.-3. 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) hydrogel and bare PGE. (a) Polymer gel with 0.1ml of aniline at 200 ppm of MB (b) Polymer gel at 200 ppm of MB, (c) Polymer gel in 120 ppm of MB, (d) Polymer gel at 40 ppm of MB at 30min swelling time. a) Polymer gel with 0.1ml of aniline in 120 ppm of MB (b) Polymer gel in 120 ppm of MB, (c) Polymer gel in 40 ppm of MB, (d) Polymer gel in 20 ppm of MB at 30min swelling time

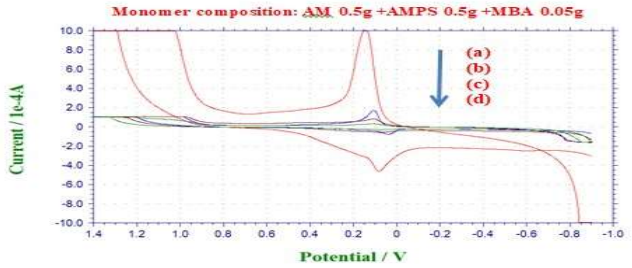

Fig.-1: Cyclic Voltammetric Response of PGEs Coated with Poly (AM-co-AMPS)/polyaniline and Poly (AM-co-AMPS) Hydrogels in Different Concentrations MB Dye at a Scan Rate of 50 mV/s

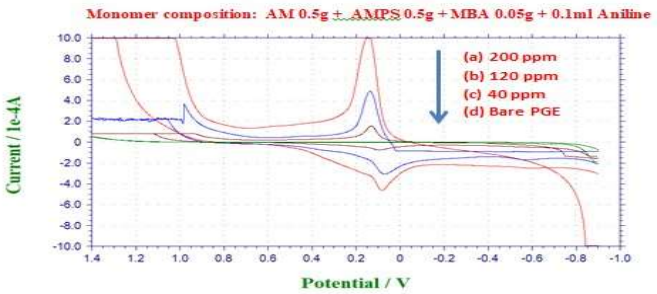

Fig.-2: Cyclic Voltammogram of PGEs Coated with poly(AM-co-AMPS)/Polyaniline Hydrogels at different Concentrations of Methylene Blue at a Scan Rate of 50mV/s.

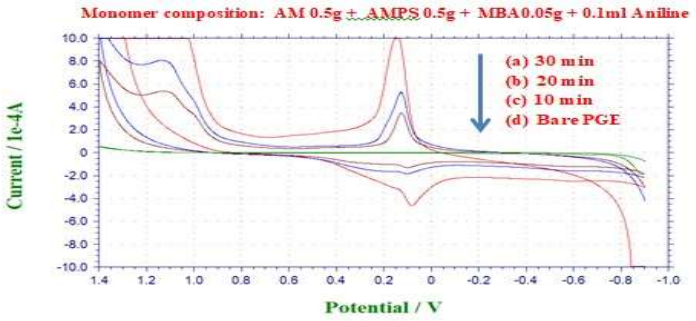

Fig.-3: Cyclic Voltammogram of PGEs Coated with Poly (AM-co-AMPS)/Polyaniline Hydrogel with different Swelling Time in 200 ppm Methylene Blue Solutions at a Scan Rate of 50mV/s.

DPV and SWV Studies

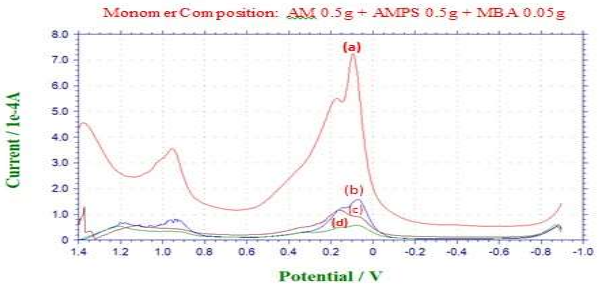

Fig.-4: DPV of PGEs Coated with P(AM-co-AMPS)/PANI and P (AM-co-AMPS) Hydrogels at the Scan Rate of 50mV/s

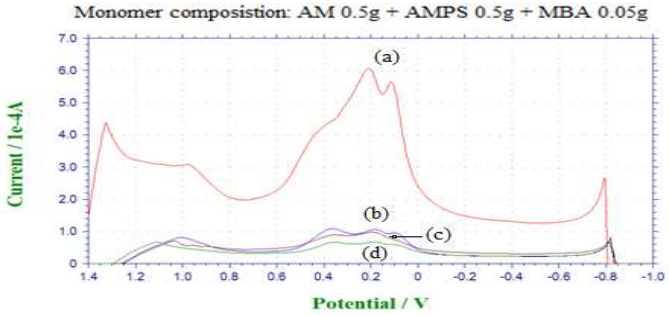

Fig.-5: SWV of PGEs Coated with P(AM-co-AMPS)/PANI and P(AM-co-AMPS) Hydrogel at the Scan Rate of 50mV/s

(a) Polymer gel with 0.1ml of aniline in 120 ppm of MB and (b) Polymer gel in 120 ppm of MB,
(c) Polymer gel in 40 ppm of MB, (d) Polymer gel in 20 ppm of MB at 30min swelling time

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 reveal that the PGE hydrogel containing polyaniline has better sensing behavior with a maximum current response of 726.9. A than the electrodes coated with hydrogels without the polyaniline and bare electrodes (Fig.-4). The peak current is shown in Table-1. In the same way, PGEs were subjected to optimized squarewave voltammetric studies. As in the DPV studies, a similar type of response was noticed but with lower peak currents. The 0.1ml aniline-based hydrogel showed a maximum peak current of 609.2 A with the electrode dipped with 120ppm of MB dye for a swelling period of 30 min. Typical squarewave voltammograms are illustrated in Fig.-5.

FTIR Analysis of the Hydrogels

The FT spectrum of P(AM-co-AMPS) and P(AM-co-AMPS)/PANI nanocomposite hydrogels are shown in Fig.-6 and 7. A broad peak corresponding to NH stretching is formed at 3434.08cm^{-1}. The peak

observed at 1645.75cm^{-1} corresponds to the C=O stretching of AM. The peaks around 1110cm^{-1},1045cm^{-1} and 620cm^{-1} correspond to asymmetric stretching of SO_2, symmetric stretching of the SO_2, and C-S stretching of AMPS respectively. The peak at 2923.53cm^{-1} is due to the CH stretching of the polymer backbone. The stretching of the C-N band is seen at around 1456 cm^{-1}.

Table-1: Voltammetric Behavior of PGE Coated with P(AM-co-AMPS) and P(AM-co-AMPS)/PANI in MB Dye: Swelling Time 30 min

Plain gel composition	Aniline (ml)	Conc. of MB (ppm)	Peak Current (µA)
0.5g AM, + 0.5g AMPS + 0.05g MBA	--	20	33.8
	--	40	82.5
	--	120	164.6
	0.1	120	726.9
	0.3	120	300.1
	0.5	120	214.7

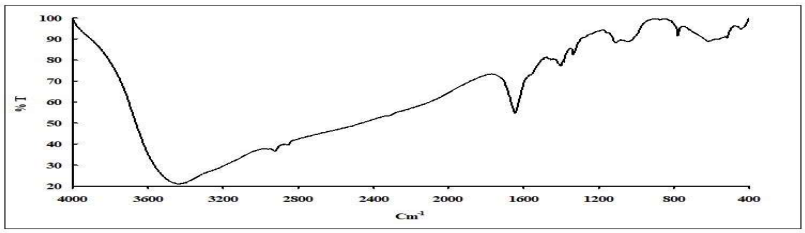

Fig.-6: FTIR Spectra of P(AM-co-AMPS) Hydrogel

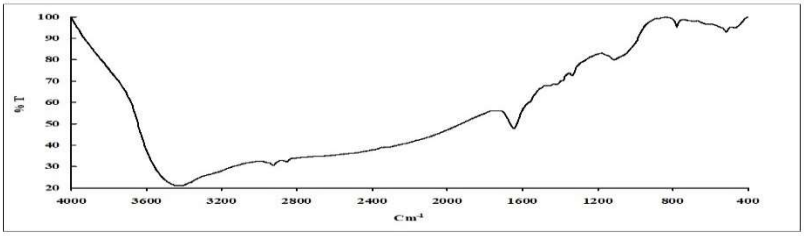

Fig.-7: FTIR Spectra of P(AM-co-AMPS)/PANI Hydrogel

XRD Analysis

The XRD patterns of the nanocomposite hydrogels are shown in Fig.-8 and 9. The 2θ values range from 10 to 80. The peak pattern of P(AM-co-AMPS) and P(AM-co-AMPS)/PANI is shown in the Fig.-9 and 10 respectively. The XRD analysis showed that the hydrogel materials are more amorphous.

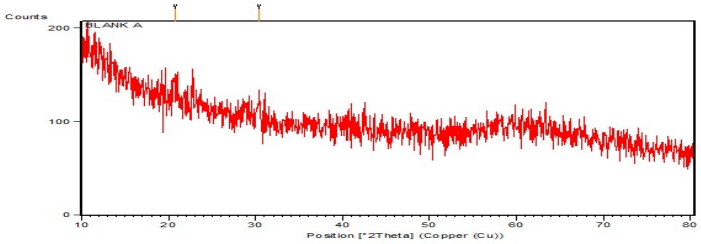

Fig.-8: X-ray Diffraction Pattern of P(AM-co-AMPS) Hydrogel

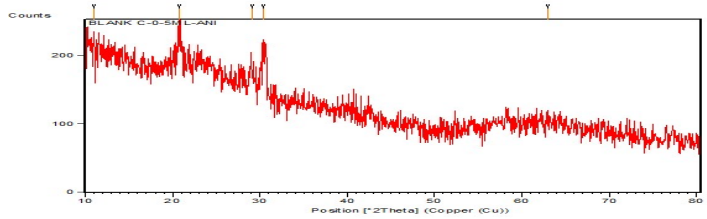

Fig.-9: X-ray Diffraction Pattern of P(AM-co-AMPS/PANI) Hydrogel

SEM Analysis

The Surface Morphology of hydrogels was studied by SEM analysis. The SEM images of the nanocomposite hydrogels are shown in Fig.-10 and 11. The images indicate the presence of nanostructured copolymers which are uniformly distributed throughout the polymer matrix.

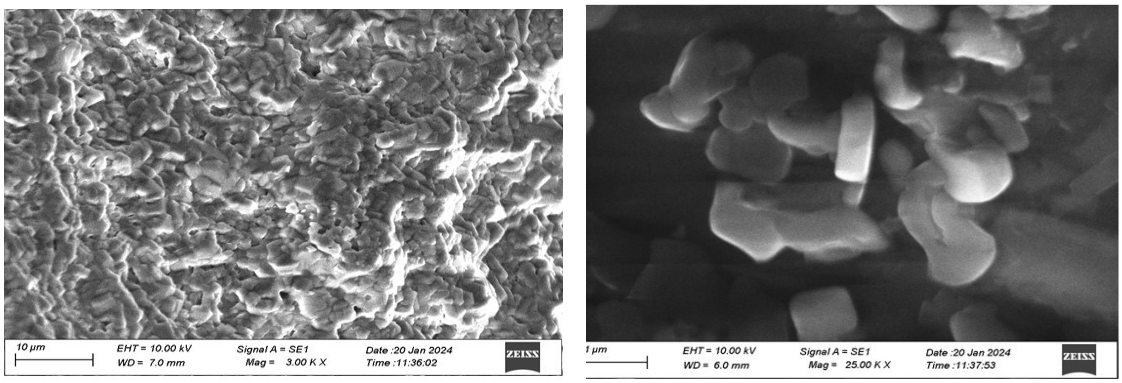

Fig.-10: SEM Analysis of P(AM-co-AMPS) Hydrogel

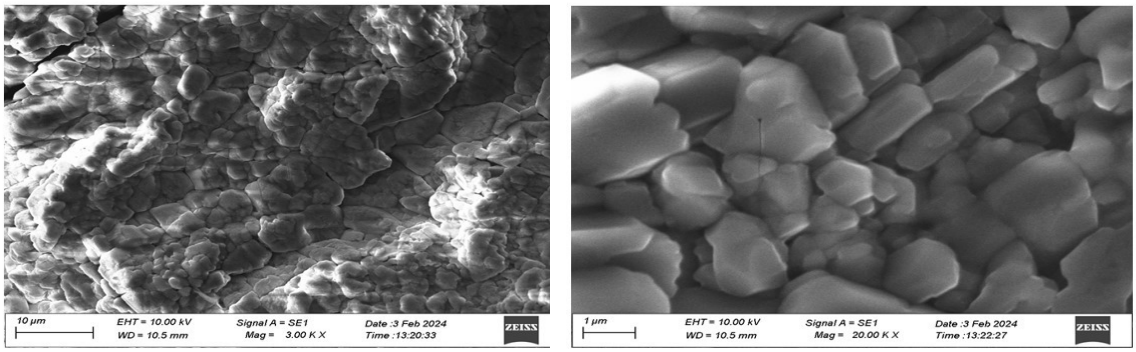

Fig.-11: SEM Analysis of P(AM-Co-AMPS)/PANI Hydrogel

SEM images of plain and aniline-based hydrogels are shown in Fig.-10 and 11. The plain P(AM-co-AMPS) hydrogel shows an undulant surface less dense and less compact structure. However, the P(AM-co-AMPS)/PANI shows a coarse, more dense, and highly compact network surface suggesting the connection and formation of a polyaniline chain within the P(AM-co-AMPS) polymer matrix with homogeneity in size and distribution.

CONCLUSION

In the present work, P(AM-co-AMPS) and P(AM-co-AMPS)/PANI hydrogels were synthesized and were used for the coating of the pencil leads which are considered 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 plain hydrogel 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 better sensing efficiency than the electrodes coated with plain and bare electrodes. Due to the excellent sensing behavior, the coated PGEs could thus potentially be a substitute for the expensive electrodes. Because of their cost-effectiveness and ease of fabrication, they may be a potential sensor for sensing environmental pollutants.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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