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Research Article

Synthesis and Characterization of Apple Pectin Acrylamide-Based Hydrogel by Thermal-Induced Graft Copolymerization

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Abstract

Potassium peroxydisulphate has been used as an initiator in an acidic medium for the preparation of Hydrogels through the interpenetrating networks chain. The grafting of hydrogel was initiated by a redox system comprising Potassium peroxydisulphate – Sulfuric acid (KPS – SA). Structural aspects of graft copolymers have been characterized by FT-IR, Viscosity Study, SEM and Swelling behaviour. Grafting has been studied as a function of the concentration of monomer, an initiator system, reaction time, reaction temperature and the amount of water. P_g (Grafting Percent) is used to express the weight increase in a monomer which is supported by the FT-IR study. Morphology of the Apple Pectin and Apple pectin–g–AAm (Pectin graft AAm Hydrogel) was examined by scanning electron microscopy (SEM) which showed a porous structure with smooth surface morphology of the hydrogel. An attempt has been made to investigate the effect of the concentration of monomer and other reaction variables on the grafting of AAm (Acrylamide) onto Pectin extracted from the apple Pomaces.

Keywords: Apple Pomaces, Hydrogel, Morphology, Percent swelling, SEM

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Introduction

The present study aims to develop cost-effective eco-friendly novel hydrogels from pectin extracted from apple pomaces, a major waste in fruit processing plants, especially in Himachal Pradesh and Jammu Kashmir and same time utilising the peel waste for the production of dry pectin. Grafting is a clean and convenient method for polymeric modification. The number of hydrogels was synthesized by graft cross-link copolymerization of acrylic acid using N, N-methylene – bis – (Acrylamide) [1]. The bifunctional and trifunctional crosslinking agents like 3 – oxopentamethylene dimethacrylate, trimethlopropane trimethacrylate (TPT) are also used to get gels with desired characteristics from these monomers. The commonly used hydrogel is Poly (2 – Hydroxyethyl methacrylates) [poly (HEMA)]. A wide variety of monomers has been successfully grafted by Misra et. al. onto starch, wool [2, 3] cellulose [4] and gelatin [5] by use of radical initiators. Pectin is a heterogeneous grouping of acidic structural polysaccharides degraded by an oxidizing agent like $KMnO_4$ and by irradiation. Biological applications [6-12], water purification [13] ion-exchange treatment [14-19] and sensing capabilities [20] of Pectin based hydrogel had already been reported in recent years.

Material and Methods

Pectin was extracted from apple Pomaces by the reflux Digestion method [21]. Acrylamide (S.D. Fines, Mumbai, India) was grafted by a redox system comprising Potassium peroxydisulphate - Sulphuric acid to get optimum polymer yield. Homopolymer separated with acetone (Reagent Grade) and extracted in Methanol.

Graft Copolymerization

Graft Copolymerization of Acrylamide onto Pectin was carried out under previously determined optimum conditions. The effect of variation of various Reaction parameters on grafting of Apple Pectin and Acrylamide was studied by keeping One Parameter Fixed. One gram of Pectin, Potassium peroxydisulphate (0.55487 x 10^{-3}M), Acrylamide (14.068 x 10^{-3}M) was immersed in a flask containing water 20 ml of distilled water for one hour at 55^0C with variable concentration of Sulphuric Acid. The optimum condition for Sulphuric acid (75.040 x 10^{-3}M) was fixed and an experiment was performed for variation of Concentration of Potassium peroxydisulphate (0.55487 x 10^{-3}M) on grafting percent.

The effect of variation of water on grafting was experimented with by taking optimum conditions for Potassium peroxydisulphate and Sulphuric acid by keeping other parameters constant. The experiment was performed in multiples by adding optimum additives to study the variation of grafting with reaction time and temperature. Grafting variation with Acrylamide was performed by fixing other additives of reaction. The homopolymer was freed from grafted Pectin by repeated extraction with Methanol. Calculation of Percentage grafting [22] and grafting parameters was done as reported by Trivedi et al. [23].

FT-IR, Viscometry, Swelling Study and SEM

FT-IR of Pectin and Pectin grafted copolymer were recorded using KBr pellets on FTIR 5100 (Thermo). Viscosity studies were carried out at different concentrations rang in water at 25^0C. Swelling studies were performed by equilibrating the pectin and grafted copolymers in an aqueous solution for 24 hr at pH 7. Samples were removed from the solutions at specific time intervals and excess water on the surfaces was absorbed by blotting with a piece of tissue paper. SEM of pectin and its grafted polymer were recorded at 5.0K, 10.0K and 25K magnification Scanning Electron Microscope Model Steroscan - 440. The results are illustrated in **Figures 1-3**.

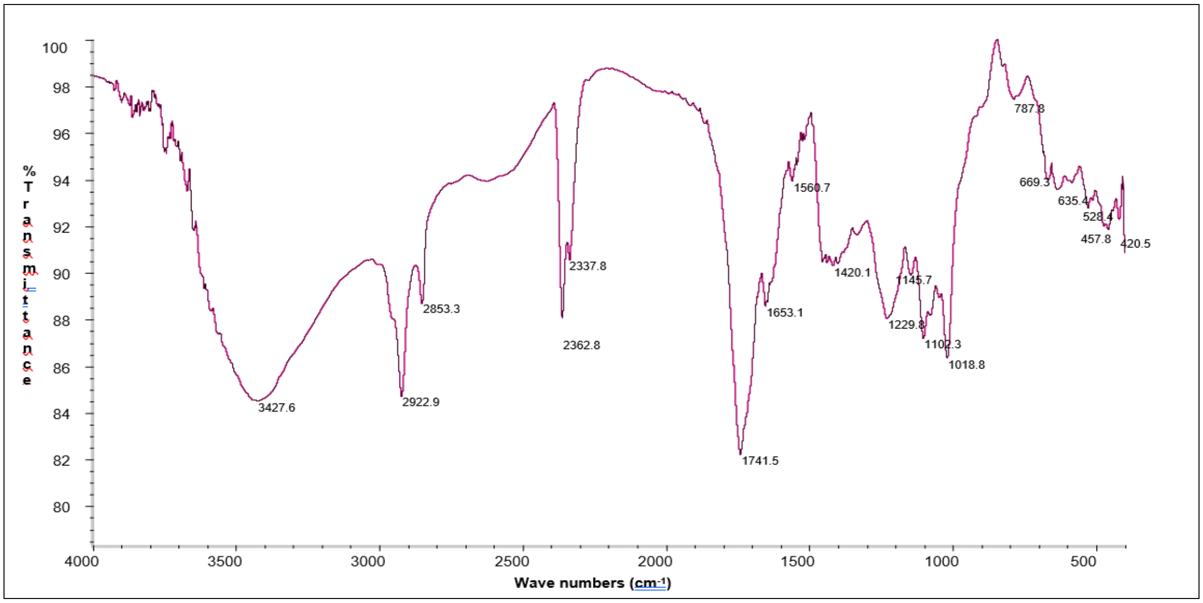


Figure 1 (a) FT-IR Spectra of Apple Pectin

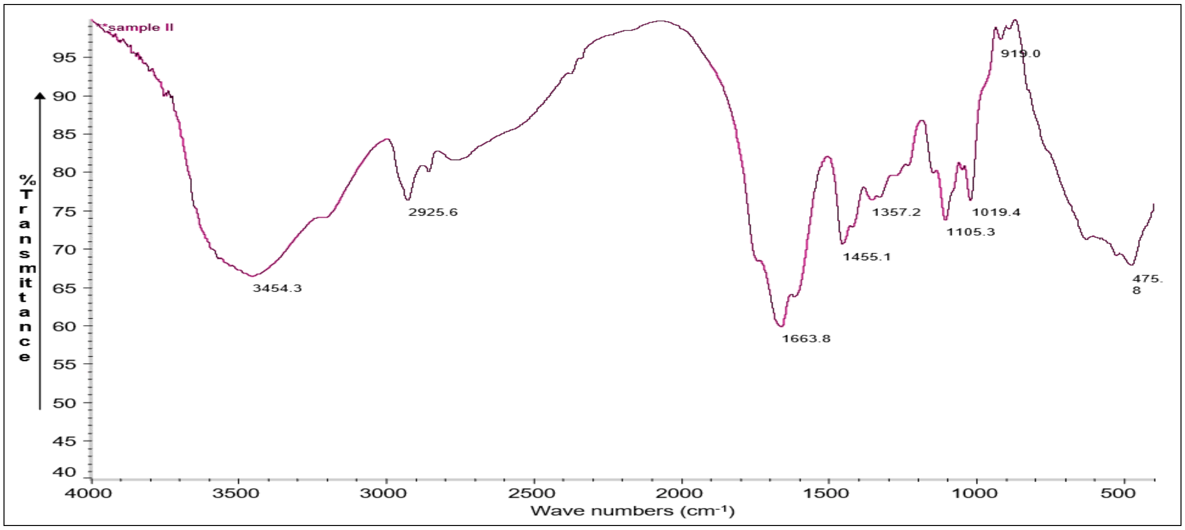


Figure 1 (b) FT-IR Spectra of Apple Pectin based Acrylamide Hydrogel (52 % grafted)

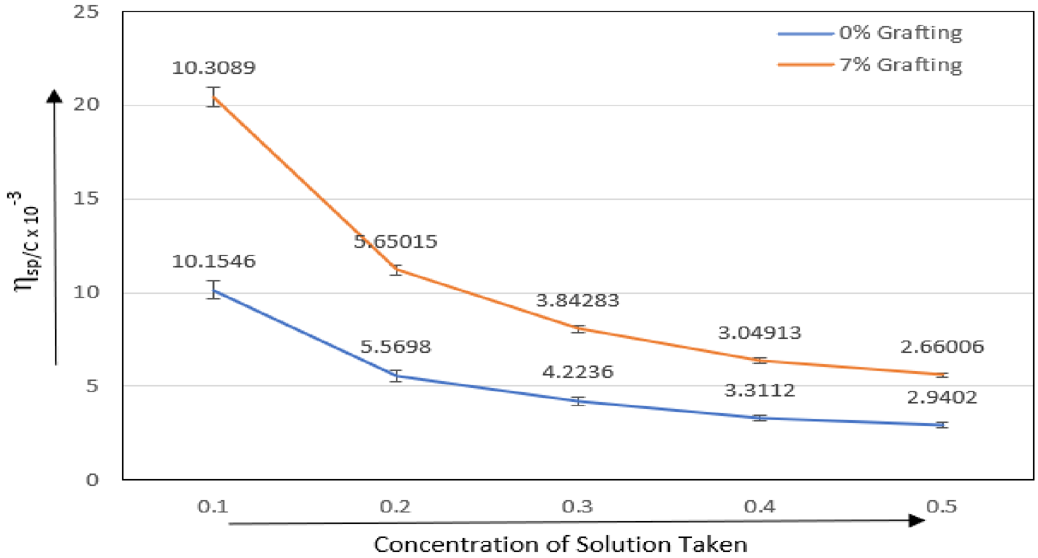


Figure 2(a) Viscosity Study of Apple Pectin graft copolymer with AAm

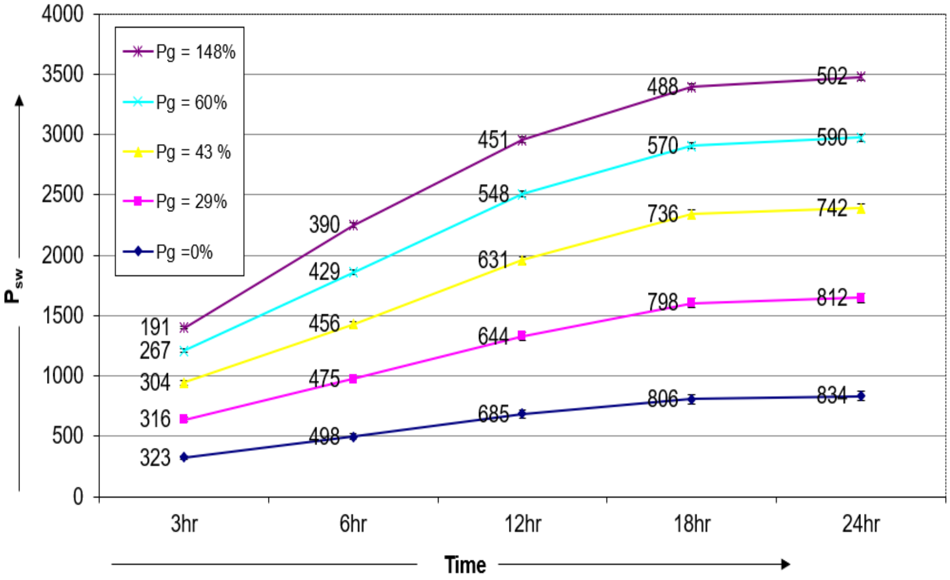


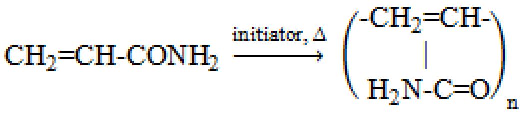
Figure 2(b) Variation of Swelling behaviour of Apple Pectin and its graft copolymer with AAm at different %grafting with time

Figure 3 Apple Pectin and its Acryl Amide Grafted hydrogel

Results and Discussion

The reactivity of redox system-initiated grafting of Pectin depends upon the availability of glycolic –OH group and consequently exchange of electrons to form free radicals. The free radical abstract hydrogen atoms from C_2, C_3 and C_6 portion of – C–H or – OH group of the un-hydro glucose unit of polymers as compared to the –OH group. The properties and yield of the grafting depend on the structure of these polymers that is unit cell spacing and degree of crystallinity. Co-polymerisation of Apple Pectin and AAm occurs by homopolymerization of the donor-acceptor complex. For grafting the following mechanism is proposed:

Reaction of Pectin with AAm



$$CH_2{=}CH\text{-}CONH_2 \xrightarrow{\text{initiator, }\Delta} \left(\begin{array}{c}\text{-}CH_2{=}CH\text{-} \\ | \\ H_2N\text{-}C{=}O\end{array}\right)_n$$

(Acrylamide) Poly – AAm (Homopolymer)

$$\text{Pectin+AAm} \xrightarrow{\text{Polymerisation}} \text{Pectin-g-AAm}$$

(Graft Copolymer)

Initiation

$$S_2O_8^{2-} + H_2O \rightarrow HSO_4^{-} + SO_4^{\cdot -} + {}^{\cdot}OH \qquad (1)$$

$$SO_4^{\cdot -} + H_2O \rightarrow HSO4^{-} + {}^{\cdot}OH \qquad (2)$$

$S_2O_8^{2-}$ decomposes un-symmetrically by reaction with water because of the influence of the H^+ ion obtained by the sulfuric Acid and involved in the breaking of the O –S bond of peroxydisulfate ion. $S_2O_8^{2-}$ can react with water and be considered the product of $SO_4^{\cdot -}$ in the rate-limiting step**.**

$$Pect - OH + SO_4^{\cdot -} \rightarrow Pect - O^{\cdot} + HSO_4^{-} \qquad (3)$$

$$Pect - OH + {}^{\cdot}OH \rightarrow Pect - O^{\cdot} + H_2O \qquad (4)$$

The yield of radicals in reactions (3) and (4) leads to the activation of trunk polymer; hence it will determine the rate of grafting, density, efficiency, and yield. Apart from these initiation between monomer (M) and backbone polymer radical affect the yield.

$$M + Pect^{\cdot} \rightarrow Pect - M^{\cdot} \qquad (5)$$

Propagation

$$Pect - OH + {}^{\cdot}M - OH \rightarrow {}^{\cdot}Pect - M - OH \qquad (6)$$

$$Pect^{\cdot} + n\,M \rightarrow Pect - (M)^{\cdot}_{n} \qquad (7)$$

$${}^{\cdot}M{-}OH + nM - OH \rightarrow HO - (M)_n - M^{\cdot} \qquad (8)$$

Termination

$$Pect - (M)^{\cdot}_{n+1} + Pect - (M)^{\cdot}_{n+1} \rightarrow Pect - (M)_{2n+2} - Pect \qquad (9)$$

$$Pect - (M) - M^{\cdot} + {}^{\cdot}OH \rightarrow Pect - (M)_{n+1} - OH \qquad (10)$$

$$2\,{}^{\cdot}OH \rightarrow H_2O + \tfrac{1}{2}\,O_2 \qquad (11)$$

The grafting percent (P_g) has been calculated by using the following relation:

$$P_g = \frac{\text{Weight of graft polymer} - \text{Weight of Polymer backbone}}{\text{Weight of the polymer Backbone}} \times 100$$

The Pg (Grafting Precent) is used to express the weight increase in a monomer which is supported by Spectroscopic methods such as FTIR. Grafting of AAm on some polymeric backbones should give a characteristics band at 1660 Cm^{-1} or in the nearby region due to the C = O absorption band. Other bands may appear in the region due to related differences in the comparative FTIR spectra of the backbone and the grafted monomer.

Analysis of FT-IR Spectra of Apple Pectin and Apple Pectin based AAm Hydrogel

FTIR spectra of Apple-based Pectin shows characteristic peaks at 3427.6 Cm^{-1}, 2922.9 Cm^{-1}, 1741.5 Cm^{-1}, 1018.8 Cm^{-1}. These peaks correspond respectively for O – H, C – H, >C = O of acid, and C – O – C stretching. The peak at 1653.1 Cm^{-1} is due to carboxylate stretching as shown in Figure 1(a). The peak assigned to – OH stretching (3427.6 Cm^{-1}) is due to the maximum association of OH groups. In 52% grafted apple-based AAm hydrogel peak is obtained at 3454.3 Cm^{-1}, 2925.6 Cm^{-1} while the extra peak at 1663.8 Cm^{-1} is due to >C = O of AAm for the polymeric network shown in Figure 1(b) and **Table 1**.

Table 1 FT-IR, Viscosity study, Swelling behaviour of Apple Pectin and Pectin-g-AAm polymer

FTIR Study of Apple Pectin and Apple Pectin based AAm Hydrogel

Polymer	**P_g**	**Characteristics Peaks**		**Remarks**
		Wave Number (cm^{-1})	**% Transmittance**	
Apple Pectin	0.0%	3427.6	84.25	O – H Polymeric Association
		2922.9	84.35	C – H Stretching
		1741.5	82.15	>C = O Str. of acid and esters
		1018.8	86.25	C – O – C stretching
		1653.1	88.25	Carboxylic Stretching
Pectin-g-AAm	52 %	3454.3	66.20	O – H Polymeric Association, N – H Stretching vibration of polyamide
		2925.6	76.30	C – H Stretching
		1663.8	59.40	>C = O of –CONH2
		1019.4	76.20	C – O – C stretching

Viscosity Study of Apple Pectin and Apple Pectin based AAm Hydrogel

Conc. of Solution taken	**0% grafting**		**7% grafting**	
	η_{sp}	**η_{sp}/C**	**η_{sp}**	**η_{sp}/C**
0.1	10.1546×10^{-4}	10.1546×10^{-3}	10.3089×10^{-4}	10.3089×10^{-3}
0.2	11.1396×10^{-4}	5.5698×10^{-3}	11.3003×10^{-4}	5.65015×10^{-3}
0.3	12.6710×10^{-4}	4.2236×10^{-3}	11.5285×10^{-4}	3.84283×10^{-3}
0.4	13.2448×10^{-4}	3.3112×10^{-3}	12.1965×10^{-4}	3.04913×10^{-3}
0.5	14.7012×10^{-4}	2.9402×10^{-3}	13.3003×10^{-4}	2.66006×10^{-3}

Swelling behaviour of Apple Pectin* and Pectin-g-AAm* Hydrogel at 25^{0}C in water

Swelling Time (S_t)	**Psw**				
	P_g = 0 %	**P_g = 29 %**	**P_g =43%**	**P_g =60%**	**P_g = 148%**
3hr	323	316	304	267	191
6hr	498	475	456	429	390
12hr	685	644	631	548	451
18hr	806	798	736	570	488
24hr	834	812	742	590	502

* Weight of the dry Sample taken = 1.00g, η_{sp} = Viscosity of Solution, η_{sp}/C = Viscosity of solution at particular concentration

Viscosity Study of Apple Pectin and Apple Pectin based AAm Hydrogel

The solution of pectin in water results in the formation of a colloidal solution. Pectin is stabilized by inter-and intermolecular attraction forces. The flexibility/rigidity of pectin plays an important part in their structure-function relationship. With the increase in concentration, a sharp decrease is observed. This behaviour is attributed to the availability of more grafting sites for initiation of graft copolymerization at higher concentrations. However, upon a further increase in the substrate concentration, an increase in the reaction medium viscosity restricts the movements of macroradicals and hence 7% graft copolymer is taken to carry out the viscosity study. The plot of reduced viscosity versus percent concentration is a curved path and does not give results according to Martin's equation. In the present study, the straight-line relationship between reduced viscosity versus concentration is not maintained.

Hence it is not possible to find the molecular weight of apple pectin. The plot of reduced viscosity versus concentration is shown in Figure 2(a) and Table 1. Figure 3 shows the Apple Pectin and Acrylamide grafted hydrogel.

Swelling behaviour of Apple Pectin and its Acryl Amide Grafted Polymer

The swelling behaviour of polymeric material is studied as a function of time. The size of the void in the polymeric backbone and the size of a solvent molecule determines the swellability relationship. In the case of pectin swollen behaviour in beginning is due to the opening of the matrix, which affects the structure and the size of the void where the diffusion of the solvent molecule takes place. With the passage of time percent swelling of the Pectin and that of grafted polymer increases and reaches the maximum where the equilibrium is established due to the balancing of the cohesive and adhesive forces in the polymer. Acrylamide grafted Hydrogel of Apple Pectin swelled in water and present swelling increases with increase in the period. The increase in grafting plays an important role in the swelling behaviour of the Apple Pectin grafted polymer. With the increase in percent grafting the swelling percent decrease. This phenomenon can easily be explained as an increase in P_g the crosslinking density increases which prevents the diffusion of a water molecule into the polymeric network along with decreasing the size of the void. The decrease in swelling is due to a change in the structure of the polymeric network. The quantity of water absorbed depends on the percent grafting on a polymeric network and as expected decreases with increasing grafting. The swelling study of the Pectin and Pectin–g–AAm Polymer conducted at pH – 7 is presented in Figure 2(b) using Table 1. Knowing the weight of the swollen sample (W_s) and weight of the dry sample (W_{ds}), the % swelling (P_{sw}) of samples was calculated by the following expression:

$$P_{sw}=\frac{W_s - W_{ds}}{W_{ds}} \times 100$$

SEM of Apple Pectin and Pectin Grafted onto Acrylamide

Scanning Electron Micrographs (SEM) of Apple Pectin and Pectin grafted Acrylamide at different magnification are presented in **Figure 4(a-c)**. The effect of grafting on the Apple Pectin polymer backbone shows the presence of clusters of grafted particles with the same magnification power.

The surface morphology of grafted polymer is greatly affected by the nature of the grafted polymer.

The effect of grafting on the Apple Pectin polymer backbone shows the presence of clusters of grafted particles with the same magnification power. In the case of Pectin, the surface morphology shows very few pores while in the AAm grafted pectin the concentration of pores increases. It is supposed that these pores are the regions of water permeation and interaction sites of external stimuli with the hydrophilic groups of the graft copolymers.

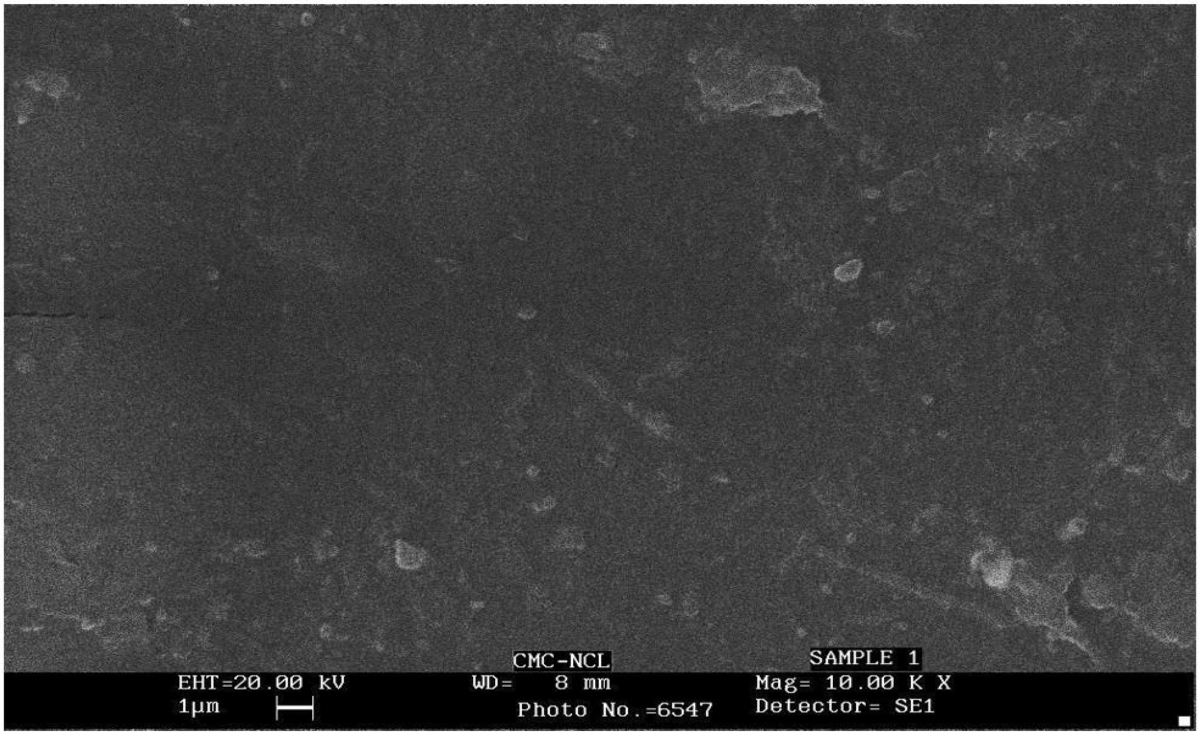


Figure 4 (a) SEM of Apple Pectin at 10 K

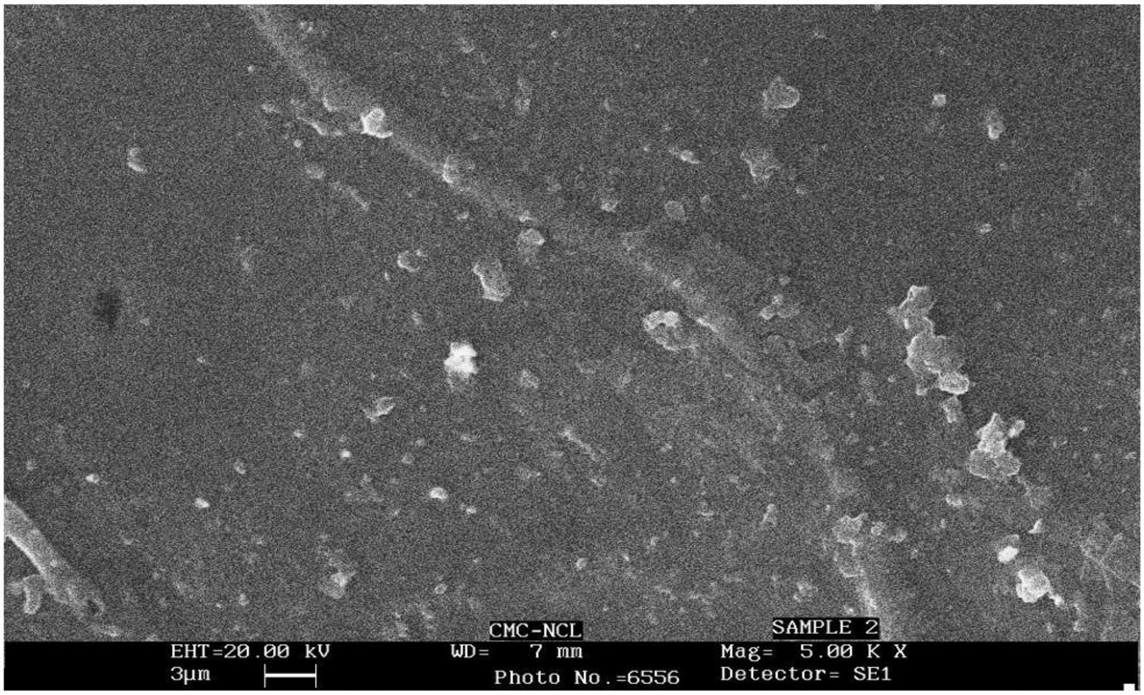


Figure 4 (b) SEM of Pectin-g-AAm at 5 K

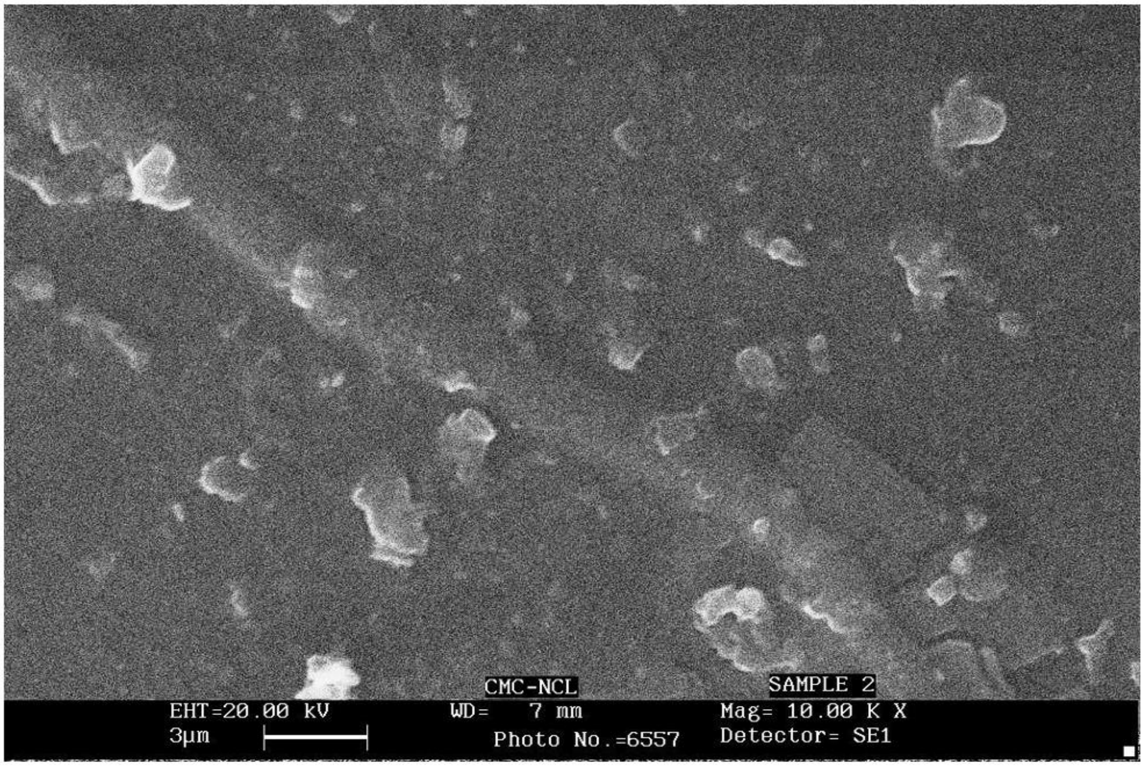


Figure 4 (c) SEM of Pectin-g-AAm at 10 K

Conclusion

A novel biopolymer-based hydrogel, pectin-g-poly(AAm) was synthesized by thermal-induced graft copolymerisation of a redox system comprising Potassium peroxydisulphate – Sulfuric acid (KPS – SA) mixtures onto Apple pectin. The Pectin-g-AAm copolymer hydrogel is useful for carrying out sorption of some common metal ions, industrial waste, and water bodies management. The grafted copolymer is more biodegradable as compared to pectin which explores the scope of reusability of the hydrogels and waste minimization in industries. FTIR and SEM spectroscopes analysis were used to prove that AAm molecules were grafted. The swelling behaviour of Apple pectin and Apple pectin-g-AAm hydrogels is also studied at different time intervals. With the passage of time percent swelling of the

Pectin and that of grafted polymer decreases and reaches the maximum where the equilibrium is established due to the balancing of the cohesive and adhesive forces in the polymer. With the increase in percent grafting on Pectin hydrogel the swelling percent decrease because crosslinking density increases which prevents the diffusion of a water molecule into the polymeric network along with decreasing the size of the void. Viscosity study of Apple pectin and Apple pectin-based hydrogel is carried out at low grafting percentage as with the increase in concentration of monomer grafting increases due to availability of more grafting sites for initiation of graft copolymerization resulting in reaction medium viscosity restricts the movements of macroradicals. The swelling behaviour of the grafted hydrogel makes it fit for the sorption of Metal ions from industrial water waste thereof.

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