

SYNTHESIS AND METAL IONS SORPTION STUDIES OF PECTIN AND PECTIN-G-AAM HYDROGELS BY THERMAL-INDUCED GRAFT COPOLYMERISATION

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ABSTRACT

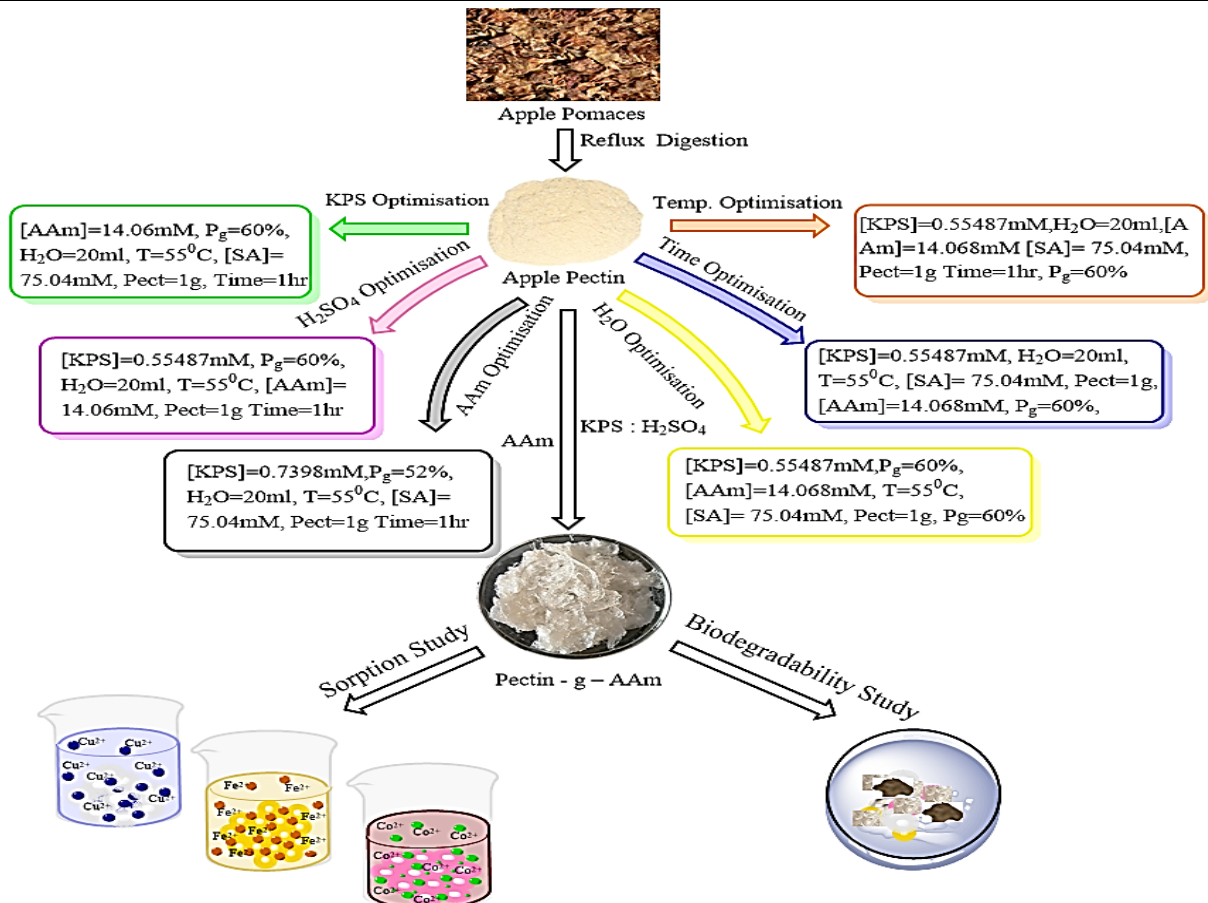
In the present study, an attempt has been made to synthesize a novel hydrogel from apple pectin extracted from Apple pomaces (waste). The hydrogel was synthesized by grafting Acrylamide (AAm) onto Apple pectin using Potassium peroxydisulphate as a free radical initiator in a redox system comprising Potassium peroxydisulphate – Sulfuric acid (KPS – SA). The optimum reaction conditions for grafting were evaluated by varying the concentration of initiator, monomer, sulfuric acid, water, temperature and reaction time. The graft copolymerization conditions were systematically optimized to achieve a hydrogel with the highest yield percent. The biodegradability of pectin-g-AAm in comparison with backbone polymer was also studied. Removing heavy metal ions by hydrogels provides an environmentally friendly, low-cost, and effective technique than the precipitation process or ion exchangers. The Sorption behaviour of the Cu⁺², Fe⁺² and Co⁺² ions by the apple pectin and the pectin grafted AAm Hydrogels on different grafting percent as a function of time were studied at a constant temperature. The salt sensitivity and cation exchange property of pectin – g – AAm polymer hydrogels marks their suitability for use in water purification and drugs.

Keywords: Acrylamide, Apple Pomaces, Biodegradability, Hydrogel, Sorption.

I. INTRODUCTION

In recent years, researchers have mainly focused on synthesizing natural three-dimensional network hydrogels with super water absorbing properties [1-3]. In today's modern world, the availability of pure drinking water is becoming the biggest challenge for the survival of civilization. Industrial effluents are the main source of contamination of natural water resources. Global industrialization results in the production of toxic heavy metal/metal ion pollutants which are resistant to biological degradation and causes various health issue in human by accumulation and heavy metal poisoning. Heavy metal ions such as Copper [4], Iron [5] and Cobalt [6] are the prominent contaminants of underground water. Various techniques such as ion exchange [7,8], resin method [9], biosorption [10,11,12], Precipitation [13,14] and absorption [15,16] etc had been developed and employed for the removal of such pollutants. Now researchers are focusing on the use of gels for water purification [17,18]. Due to the biodegradability of hydrogels in natural conditions, they are good absorbents for environmental pollutants. For the sorption of Metal ions, the active function group is required on the backbone of the polymer and Grafting [19] is a simple technique to incorporate this. Pectin [20] is generally extracted from citrus fruits and Apple pomaces [21]. Pectin is an anionic plant polysaccharide of d-galacturonic acid having $\alpha(1,4)$ glycosidic linkages.

The "shifted" egg-box model of the metal binding mechanism formed between two neighbouring chains, stabilized by van der Waals interactions and hydrogen bonds in addition to electrostatic interactions is responsible for the association of pectin with metal ions. The chemical structure of hydrogel plays a vital role in the removal of metallic pollutants. polymeric hydrogels with amines-like functional groups can be used as complexing agents for the removal of metal ions in an aqueous solution [22].



II. MATERIAL AND METHOD

Material

Apple Pomaces used to extract pectin were of HPMC (HIMACHAL PRADESH MARKETING CORPORATION) own fruits processing plant at JADOL Sunder Nagar. Acrylamide (S.D. Fines, Mumbai, India), Potassium peroxydisulfate (E. Merck, Mumbai, India), and Sulfuric Acid (Nice Chemicals, Cochin, India) were of analytical grade and used without further purification. Distilled water is used for the preparation of hydrogel and other experimental work.

Copper Sulphate (SD fine Chemicals), Ferrous Sulphate (SD Fine Chemicals) and Cobaltous Chloride (Nice Chemicals) were used as received for the preparation of standard solutions in water. All weights were taken on the AC-200 balance having minimum readability of 1.0 mg.

For the biodegradability study, the Garden soil was taken and characterized for pH, moisture content, and water holding capacity by using a standard Soil Testing Kit.

Preparation of Apple Pectin

Pectin was extracted by the reflux Digestion method. The apple Pomaces were taken, dried in the open air, crushed and ground to a fine powder. About 5g of Pomaces powder was taken in a round bottom flask containing Citric acid of pH ≈ 2.5 (5g/100ml) and refluxed at 97°C for 110 minutes in a solvent: solute (1:50). The hot extract was pressed in a cheesecloth bag and hot Conc. The Juice (called pool) was cooled to 4°C. The cooled juice was added to isopropyl alcohol in 1: 2. The mixture was stirred for 5 minutes and left undisturbed for 60 minutes. The pectin floats over the alcohol-water mixture and was separated with the help of cheesecloth shocked in isopropyl alcohol. The gel thus obtained was dried at 55°C in a hot air oven with a constant supply of air till the constant weight was obtained. The dried mass was crushed to a fine powder in a mortar and pastel. The powder thus obtained was stored away from moisture, heat, and light and labelled as Pectin.

Preparation of Hydrogel

Three necked glass reactors fitted with a condenser, thermometer and motor stirrer containing distilled water (20 ml) and Apple pectin (1.0 g, as extracted above) were placed in a thermostated water bath for 30 min at 55°C.

After 30 min continuous stirring Apple pectin dissolves resulting in a homogeneous mixture. Potassium peroxydisulphate - Sulphuric Acid mixture was added with continuous stirring followed by the addition of Acrylamide. The reaction mixture was continuously stirred for 30 min and allowed to stand. After one hour a gelation material obtained was treated with sodium hydroxide for decarboxylation of the acid group. The gel product thus obtained was repeatedly extracted with 100 mL Methanol for 1 hr. After 24hr the dehydrated gel was taken in filter paper to observe additional water molecules and dried in an oven at 30°C for 2 hr. Ground the novel specialty hydrogel (Pectin - g - AAm) and stored it away from moisture, heat, and light.



Figure 1: (Pectin - g - AAm hydrogel)

Separation of homopolymer

In the synthesis of Pectin - g - AAm, the homopolymer was separated from the reaction mixture with acetone and was dried under a vacuum. The dried gel was solubilized in the water again and digested for ten minutes and then lyophilized with acetone and dried again. Xerogel s repeatedly treated with water and stirred for one hour, the sol fraction of Hydrogel if any was removed by extracting in methanol. The above process was repeated till the constant weight of the grafted Hydrogel is not obtained. The grafting percent (P_g) has been calculated by using the following relation [19]:

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

The P_g (Grafting Percent) is used to express the weight increase in a monomer.

Metal ion sorption Study

Sorption study of Apple pectin and pectin-g-AAm grafted hydrogels was carried out by emerging the weighted sample (20 mg) of apple pectin and pectin-g-Aam hydrogel in 20 ml solution of Cu^{2+} , Fe^{2+} and Co^{2+} salts for the different intervals of time. The filtrates of the solution were analyzed for the concentration of the rejected ions on Spectrophotometer - 301(MS Electronics). Using the maximum limit of the instrument the filtrate was diluted to meet the range of the instrument. The metal ion sorption study was carried out near 6.24 pH because at higher pH there is a probability of the formation of precipitates of ions [23]. The percent metal ion uptake (P_u) is expressed as [24]:

$$P_u = \frac{\text{amount of metal ions Sorbed}}{\text{total amount of metal ions present}} \times 100$$

Biodegradability Study

The soil burial method was used for the biodegradation study of apple Pectin polymer. 1.0 g of the Apple Pectin and Pectin - g - AAm hydrogel of Apple pectin was taken, mixed with the characterized soil taken in a vase and placed 5 cm from the surface of top soil for the particular time period and exposed to the natural conditions. After the given time period the hydrogel was taken out and dried with tissue paper first and then in a hot air oven till the constant weight is obtained.

III. RESULTS AND DISCUSSION

The reactivity of redox system-initiated grafting of Pectin depends upon the availability of glycolic -OH group and

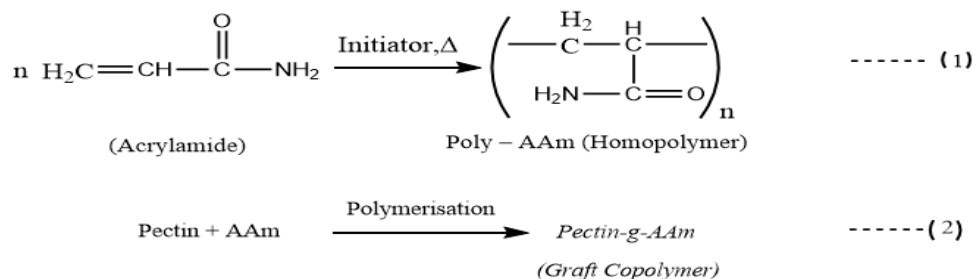


Figure 2(a): (Reaction between acrylamide and pectin)

consequently, the exchange of electrons forms free radicals. The free radical abstract hydrogen atoms from the C₂, C₃ and C₆ portion of the -C-H or -OH group of the un-hydro glucose unit figure 2(b) of polymers [25] 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 [26]. The reaction between acrylamide and pectin is shown below in figure 2(a)

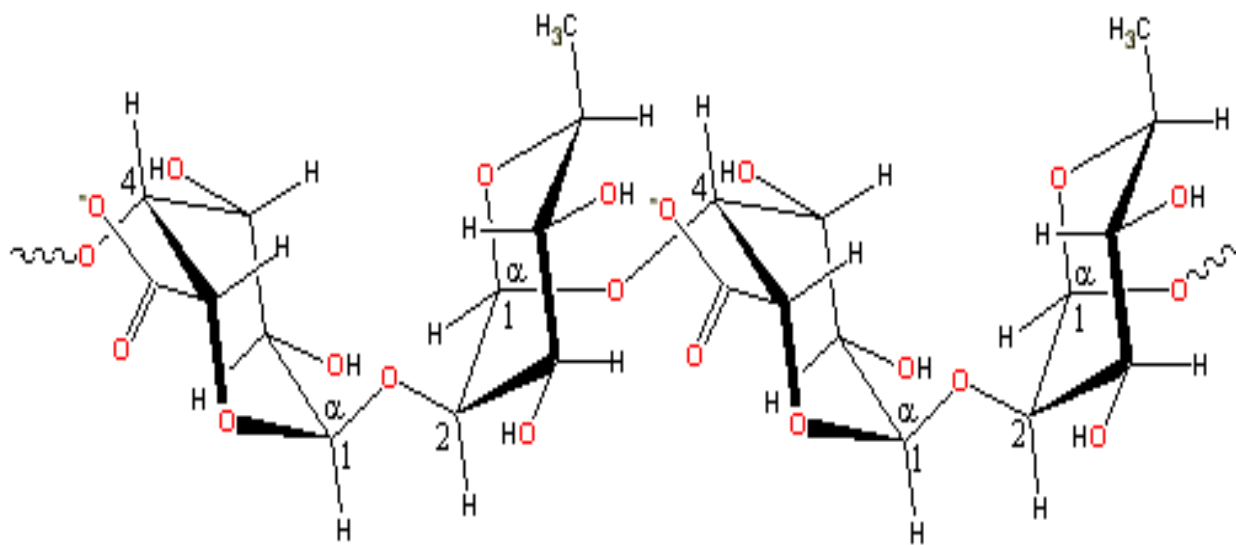


Figure 2(b): Structure of Pectin

Effects of different parameters affecting the grafting of AAm onto Apple Pectin studied have been evaluated on the yield of the network formed.

Effect of Initiator Concentration

It follows from Table 1.0 and Figure 2.1 that the P_g was studied as a function of the concentration of KPS (varied from 0.18495 x 10⁻³ M to 0.92479 x 10⁻³ M) at a constant concentration of Sulfuric Acid and AAm. Other reaction parameters like the amount of water, reaction temperature, Concentration of Sulphuric Acid and reaction time were fixed. With the increase in the concentration of Potassium persulphate, the percent grafting first increases and reaches to the maximum value of P_g = 60 % at (KPS = 0.55487 x 10⁻³ M) then starts decreasing.

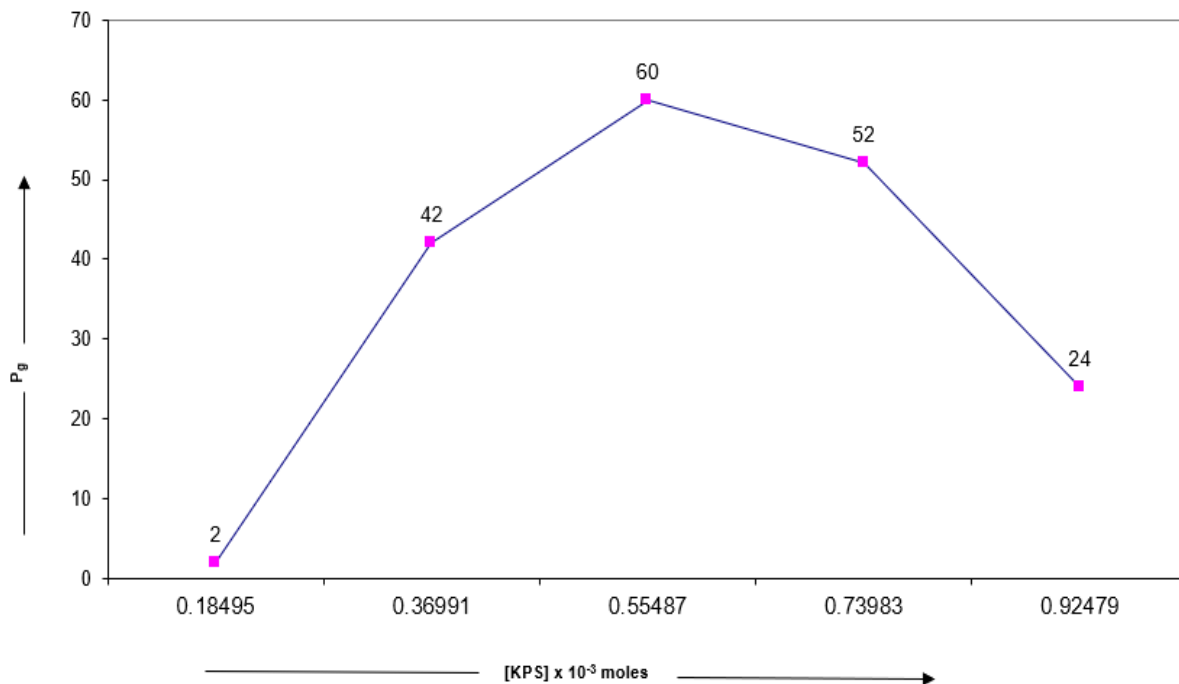


Figure 3: (Effect of Concentration of KPS on the Percent grafting at 55°C [Pectin] =1g, [H₂O] = 20 ml)

An increase in the concentration of the initiator leads to the creation of more active sites on the backbone of Pectin polymer resulting in an increase in grafting on the polymeric backbone. At higher concentrations of initiator, many macroradicals chains from monomer get initiated, resulting in the linking of different polymeric chains with one another, causing the decrease in reaction sites and hence responsible for the decrease in percent grafting.

Effect of Sulfuric Acid Concentration

Taking optimum KPS concentration (KPS = 0.55487 x 10⁻³M) the concentration of Sulfuric Acid was varied keeping other reaction parameters constant. From table 1.0 and Figure 2.2, it follows that the maximum Pg was obtained at 75.040 x 10⁻³M of sulfuric acid. The increase in the concentration of Sulphuric Acid results in a change in the pH of the reaction medium. Initially, the increase in the concentration of Sulphuric acid produced the hydrogen ions in the solution which

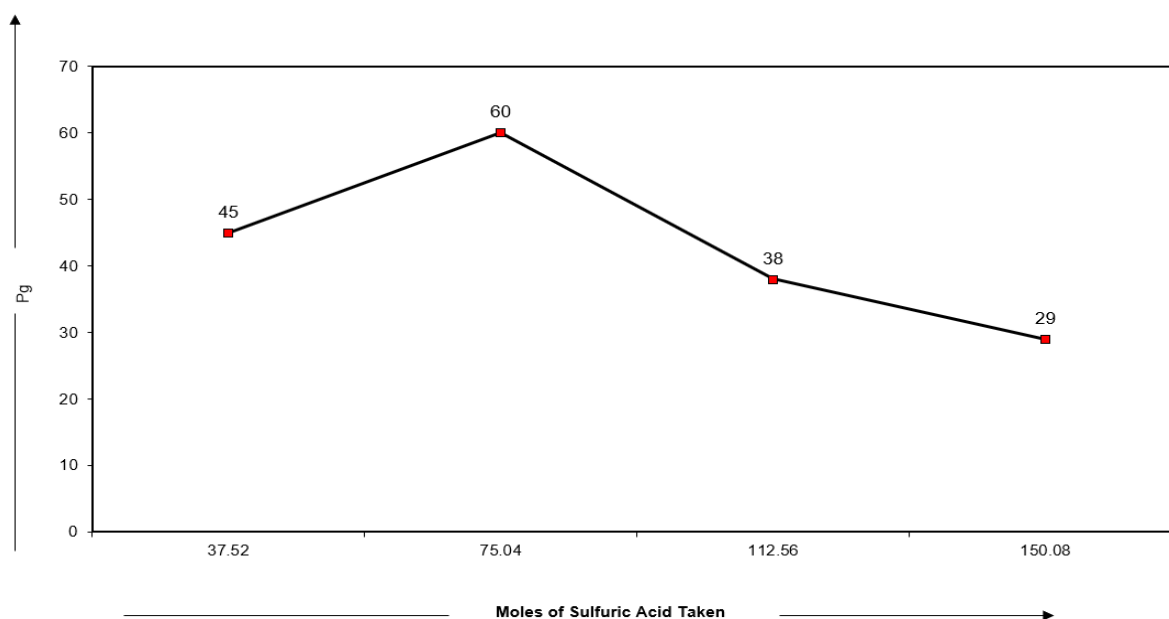


Figure 4: (Variation of Percentage grafting with Concentration of Sulfuric Acid)

catalysis the polymerisation by thermal decomposition of potassium persulphate [27] and hence the P_g increases. But with the further increase in acid concentration in reaction, unsymmetrical cleavage of O-O bond of persulphate ion took place which is responsible for acquiring a negative charge on growing polymer. The increase in electrostatic repulsion between growing radicals hinders the grafting on the polymer backbone and also there is the formation of AAm macro radicals due to self-polymerisation hence a decrease in pH, results in a decrease in the percent grafting.

Effect of monomer Concentration

The concentration of monomer is the prime factor responsible for the grafting of the polymeric chain. When the monomer concentration varied from $7.034 \times 10^{-3}M$ to $42.205 \times 10^{-3}M$, it was observed that the P_g increases continuously from 0.7% with the minimum and increased with the increase in the concentration of monomer as shown in Figure 2.3 and table 1.0 but with the higher concentration of monomer, the separation of homopolymer becomes difficult due to the formation of homopolymer. The maximum percent grafting (P_g) was 196.00, But the optimum condition was considered to be 14.068×10^{-3} Moles, at this concentration the separation of homopolymer from the graft polymer was easier due to the low concentration of homopolymer as compared to the concentration of graft copolymer. At very high monomer concentrations the reactions initiated largely, resulting in an increase in the grafting.

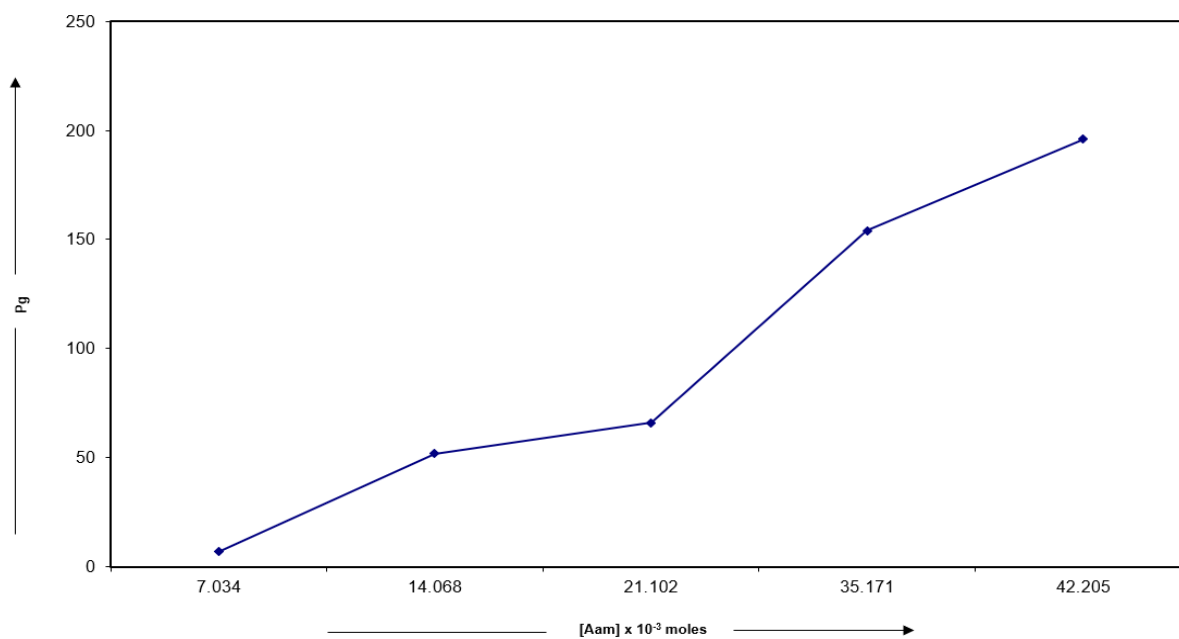


Fig 5: Effect of Monomer Concentration on Percent Grafting at 55°C Temperature

Effect of amount of Water

From table 1.0 and Figure 2.4, it is evident that the variation in the amount of water from 10 ml to 30 ml leads to an appreciable change in the grafting of the polymeric backbone. Initially, it has been observed that with the increase in dilution, the P_g increases and attains the maximum percent grafting (P_g) 60 at 20 ml, further dilution results in a decrease in the grafting. With the initial increase in dilution, the accessibility of reaction sites on the polymeric backbone by monomer increases. At 20 ml dilution, maximum active sites get occupied by the monomer and hence maximum grafting was noticed. Both backbone and monomer are hydrophilic which increases the accessibility of growing macro radicals to the active sites. In the light of solubility of both backbone polymer and monomer in the aqueous medium, the amount of water becomes very important at the optimum amount of water. Hence at a lower amount of water, the lower accessibility of monomer and its interaction with polymer takes place and the same is enhanced when more water is added. However, further dilution of the reaction system leads to a sharp decrease in graft yield as the accessibility of initiation species to both monomer and backbone polymer is restricted. The increased amount of water also restricts the accessibility of the monomer molecule as well as growing polymeric chains to the active sites on the backbone polymer due to the dilution effect leading to a decrease in P_g .

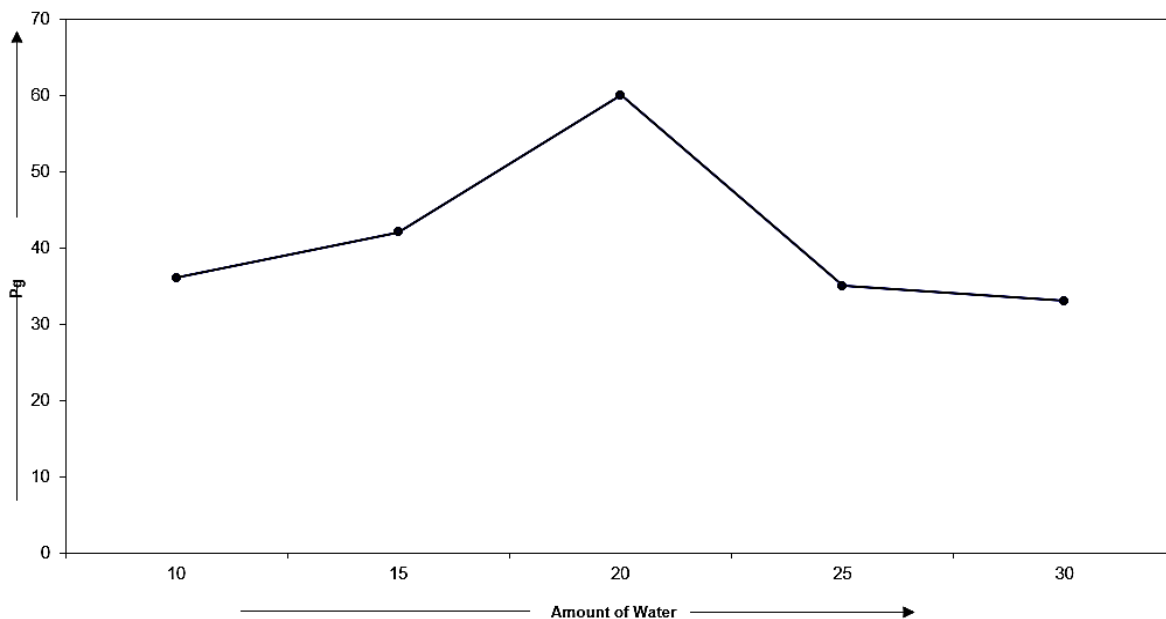


Fig 6: Variation of Percentage grafting with the amount of water

Effect of Reaction Time

After finding the optimum condition for the concentration of initiator, monomer concentration and amount of water, the optimum condition for the reaction time was evaluated by keeping the other known optimum reaction system parameters constant. The reaction time was varied from 0.5hr to 1.5hr and it was found that at a small reaction duration, the P_g was low and increased with the increase in reaction time. The maximum P_g of 60% was obtained when the reaction time was 1.0hr. The effect of reaction time was shown in table 1.0 and figure 7. At other optimum conditions of initiator, monomer concentration, amount of water, the optimum condition for time dependency is 1.0hr.

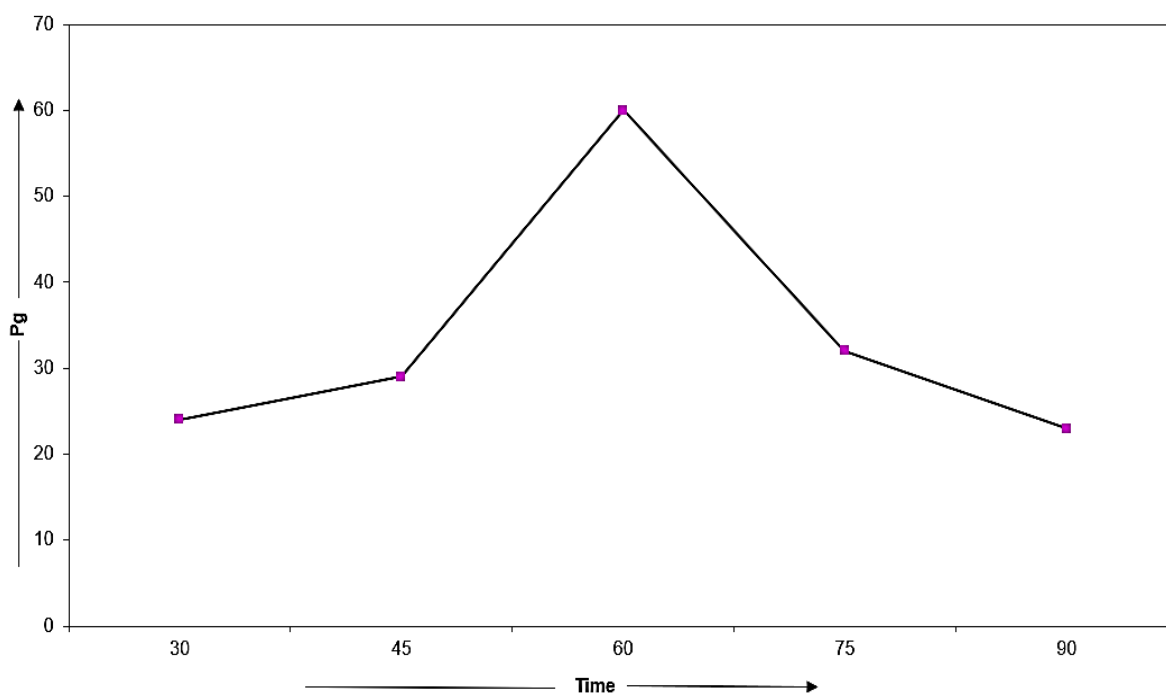


Fig 7: Variation of Percentage grafting with Time

The decrease in grafting with time is due to a decrease in the accessibility of monomer free radicals to each other. The formation of homo-polymers by monomers rather than graft copolymers is another factor responsible for the decrease in grafting.

Effect of Reaction Temperature

The effect of the variation of temperature on percent grafting is shown in table 1.0 and Figure 2.6. The reaction at optimum conditions for initiator, Monomer concentration, amount of water and the time was carried out at different temperatures varying from 45°C to 65°C to evaluate the optimum reaction temperature. The variation of temperature was studied by the reaction of the same system at 45°C, 50°C, 55°C, 60°C and 65°C. Initially, with the increase in temperature percent grafting increases and reaches the maximum at 55°C and with a further rise in temperature, the percent grafting starts decreasing. The role of temperature on the grafting induced by chemical initiation emanates from the supply of higher energies required for the acceleration of the polymerization process. Higher temperature leads to accelerate the decomposition of Redox system and more free radicals are generated. But after the optimum temperature the further increase in temperature, grafting efficiency decreases due to increased intensity of side reactions as reported earlier by Chauhan et. al [28].

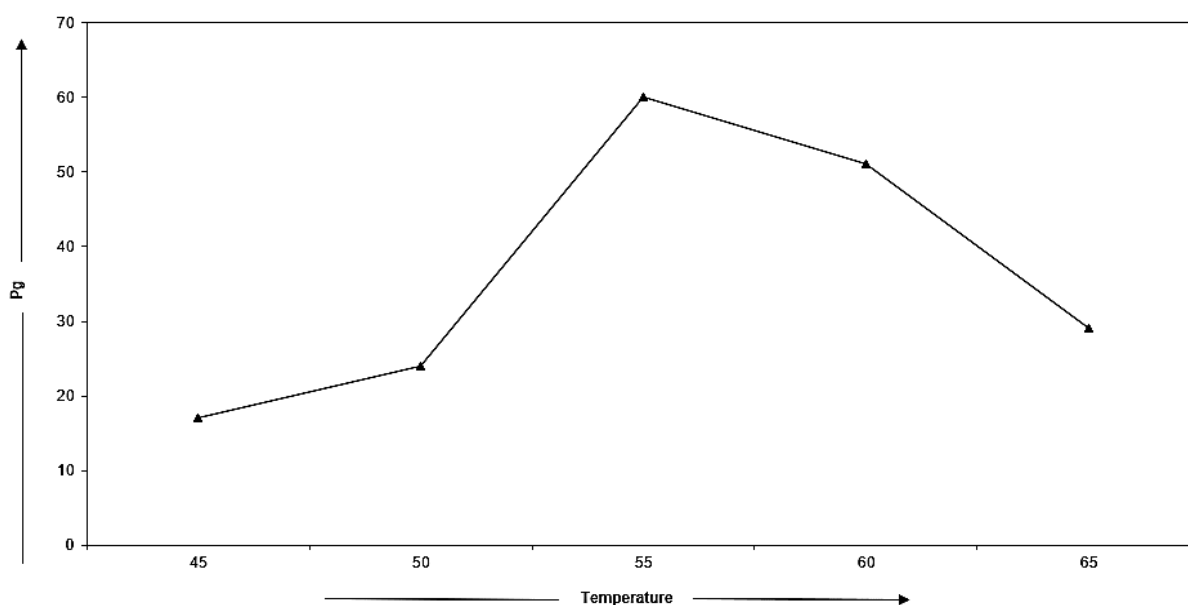


Fig 8: Variation of Percentage grafting with Temperature

Table 1.0 Effect of variation of Various Reaction Parameters on P_g of Apple Pectin #

Sr. No.	KPS (x 10 ⁻³) M	H ₂ SO ₄ (x 10 ⁻³) M	AAM (x10 ⁻³) M	Amount of H ₂ O (ml)	Reaction Time (hr)	Reaction Temp (°C)	P _g
01	0.73983	75.040	07.034	20.00	1.00	55.0	07
02			14.068				52
03			21.102				66
04			28.137				148
05			35.171				154
06			42.205				196
07	0.18495	75.040	14.068	20.00	1.00	55.0	02
08	0.36991						42
09	0.55487						60
10	0.73983						52
11	0.92479						24
12	0.55487						36

13				15.00			42
14				20.00			60
15				25.00			35
16				30.00			33
17					0.50		24
18					0.75		29
19	0.55487	75.040	14.068	20.00	1.00	55.0	60
20					1.25		32
21					1.50		23
22						45.0	17
23						50.0	24
24	0.55487	75.040	14.068	20.00	1.00	55.0	60
25						60.0	51
26						65.0	29
27		37.520					45
28	0.55487	75.040	14.068	20.00	1.00	55.0	60
29		75.040					38
30		112.560					29

#Weight of Apple Pectin = 1.00g

Sorption study of Cu²⁺, Fe²⁺ and Co²⁺ ions

In comparison to the conventional ion exchangers, the Hydrogels of the natural polymers are better for metal ion sorption because of their selective nature. The Sorption behaviour of the Cu²⁺, Fe²⁺ and Co²⁺ ions by the Apple Pectin and Pectin -g – AAM Hydrogel on different grafting percent as a function of time is presented in Table 2.0.

With the increase in the grafting on the Apple Pectin by the AAm the % metal ions uptake (Pu) of the Cu²⁺ ion increases. at low concentrations, the metal ion uptake of the Cu²⁺ ion increases with the passage of time. After 72hr the Cu²⁺ metal ion uptake starts decreasing in apple Pectin and in the low-grafted apple Pectin hydrogel while in the higher-grafted hydrogel, it appears almost constant. The increase in the uptake of metal, in the beginning, is due to the

Table 2.0 Metal ion Sorption Study for Pectin (20mg) and its Graft copolymer for different Metal Ions at pH = 6.24

Metal Ion	Time (hr)	Pectin	17% grafted	32% grafting	51% grafting	for 66% grafting
Sorption of Cu ²⁺	12	16.95	18.30	18.95	20.00	20.15
	24	18.00	18.35	19.00	20.40	20.55
	48	18.50	18.95	19.75	20.70	19.80
	72	20.00	19.30	20.65	20.30	20.50
	96	18.75	19.45	19.55	20.30	20.50
Sorption of Co ²⁺	12	23.15	23.93	25.08	23.03	24.08
	24	23.75	23.78	24.98	23.38	24.08
	48	23.95	23.88	24.73	24.38	25.18

	72	24.05	23.53	24.23	24.38	24.08
	96	24.3	24.58	23.78	24.68	24.53
Sorption of Fe ²⁺	12	20.89	22.09	22.94	23.44	23.19
	24	20.84	22.29	22.44	23.84	23.69
	48	21.29	22.59	22.44	24.14	23.19
	72	22.24	22.24	22.44	23.89	23.74
	96	21.34	21.14	23.19	23.24	23.59

imbalance in the hydrophilic and hydrophobic forces. The increase in the uptake of the metal ion with the increase in the grafting is due to an increase in the high complexing ability of the Ligand attached to the parent apple Pectin.

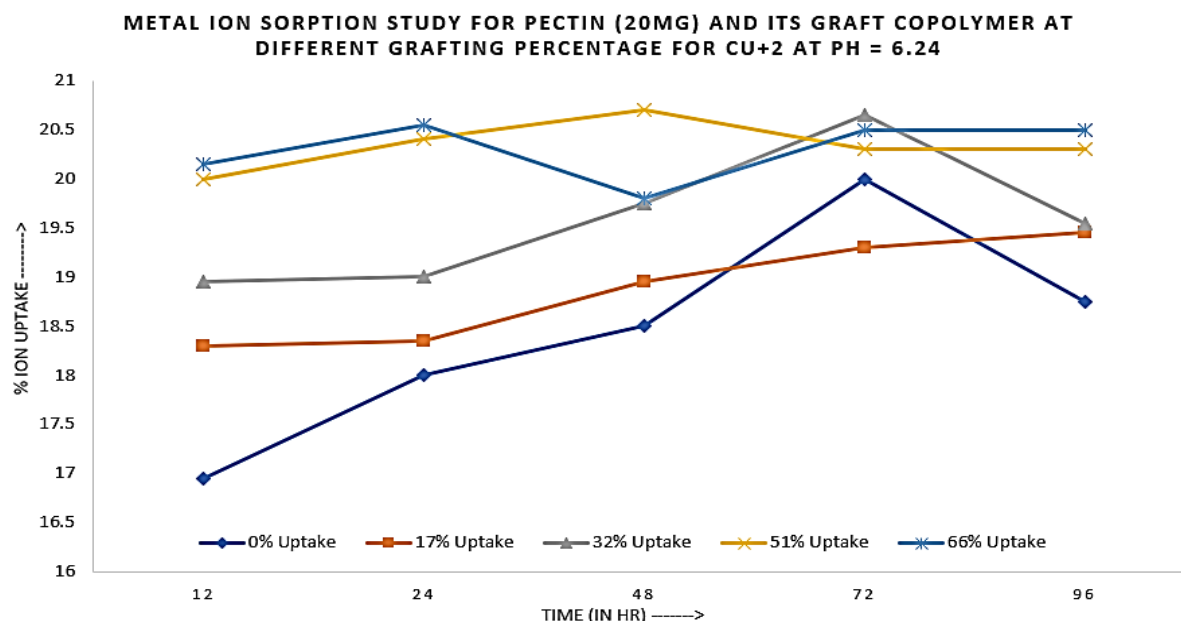


Figure 9: Sorption of Cu²⁺ ions on pectin and its graft copolymer at 6.24 pH

In the case of Co²⁺, the variable metal ions uptake trend is observed in low-grafted Apple Pectin hydrogel. For zero-grafted hydrogel, the maximum uptake is observed at 72hr and then it starts decreasing. However, for 17% grafting the uptake of metal ion initially increases to a maximum at 48hr and then starts decreasing and becomes constant. The increase in the metal ion uptake for Co²⁺ is similar to that of Cu²⁺ ion, but in the case of the Fe²⁺ ion the uptake of the metal ions is higher than in comparison to the Cu²⁺ ion. The variable metal ions uptake trend in the case of Fe²⁺ is observed in low-grafted Apple Pectin hydrogel and the variable trend is shown in figure 9.

METAL ION SORPTION STUDY FOR PECTIN (20MG) AND ITS GRAFT COPOLYMER AT DIFFERENT GRAFTING PERCENTAGE FOR COBALT ION AT PH = 6.24

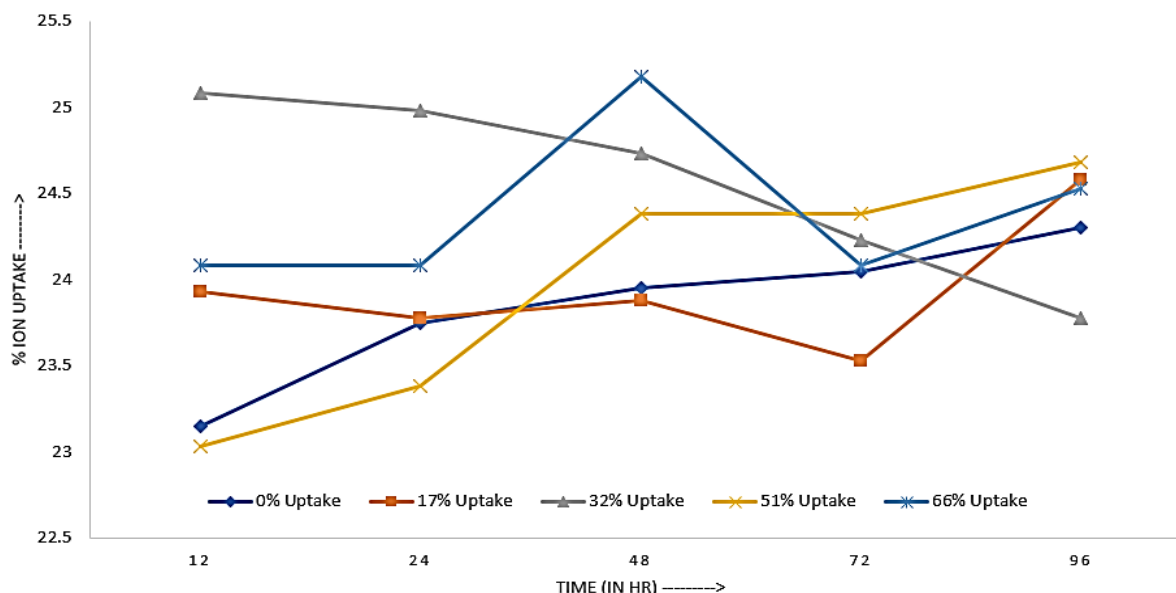


Figure 10: Sorption of Co^{2+} ions on pectin and its graft copolymer at 6.24 pH

For zero-grafted hydrogel, the maximum uptake is observed at 72hr and then it starts decreasing. However, for 17% grafting the uptake of metal ion initially increases to a maximum at 48hr and then starts decreasing till it becomes constant. The increase in the metal ion uptake has been observed is similar to that of Cu^{2+} ion, but in the case of Fe^{2+} ion the uptake of the metal ions is higher than in comparison to the Cu^{2+} ion.

METAL ION SORPTION STUDY FOR PECTIN (20MG) AND ITS GRAFT COPOLYMER AT DIFFERENT GRAFTING PERCENTAGE FOR FE+2 AT PH = 6.24

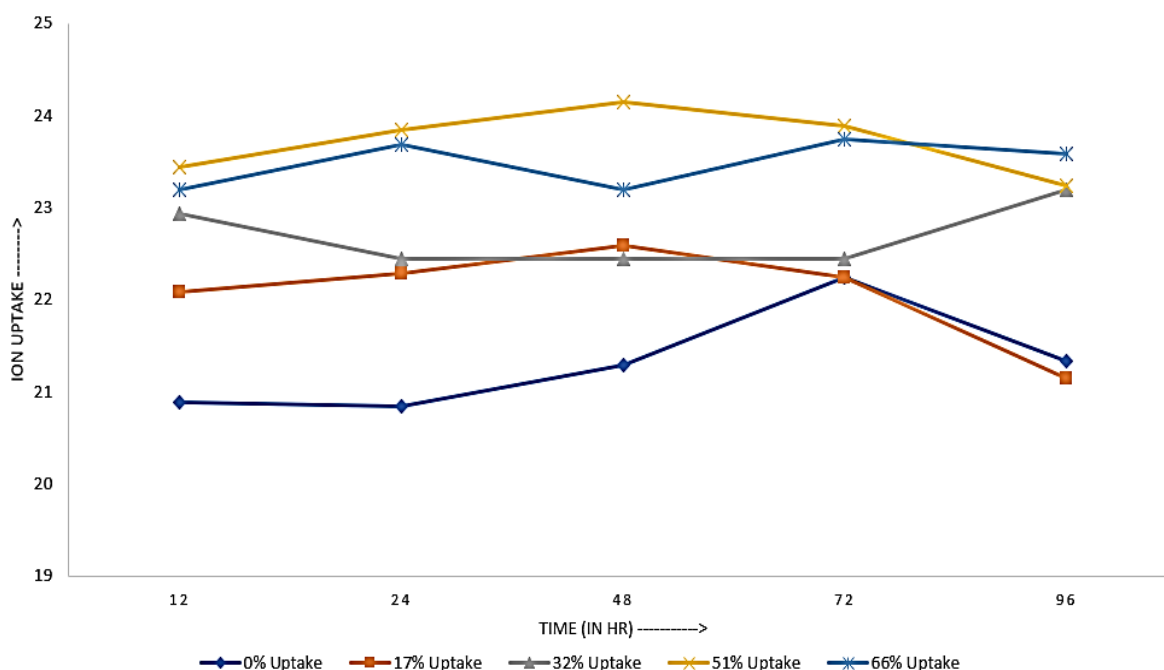


Figure 11: Sorption of Fe^{2+} ions on pectin and its graft copolymer at 6.24 pH

From the sorption study of Pectin, it is observed that the sorption of Co^{2+} ions is appreciable, followed by Fe^{2+} and then Cu^{2+} ions. The maximum sorption of cobalt is obtained at 72 hr while in the case of Pectin - g - AAm the sorption increases with an increase in P_g . Regarding Iron and copper ions sorption the maximum sorption was observed for 51% grafted Pectin - g - AAm hydrogel at 48hr while sorption of Cobalt ion is maximum for

66% grafting. The variable trend for the sorption of metal ions to different % grafted (P_g) hydrogels is attributed due to the formation of particular-sized cavity hydrogel and also to the size of metal ions. The increase in sorption of metal ions with time is because of the fact that Pectin – g – AAm hydrogel is hydrophilic in nature and it swelled with the passage of time as reported in the previous paper [25] which leads to an increase in the particular sized cavity in polymeric network and hence sorption of metal ion increases. In some cases, there is a decrease in metal ions sorption with time after reaching the maximum P_g . The decrease in P_u (% uptake) is due to rapturing of the polymeric network of the hydrogel. With the passage of time more water molecule gets associated with the polymeric network resulting in the weakening or breaking of bonds formed in hydrogel and consequently adsorbed metal ion get released from the polymeric network.

Biodegradability study

The biodegradability study of apple pectin and its grafted acrylamide hydrogel was carried out by characterizing the soil for pH, moisture content, and water-holding capacity at room temperature. The average value of moisture content of soil and water holding capacity was 5.71, 28.35 % and 80.73 %. The characterized soil was then used to carry out the biodegradability of apple pectin and Pectin – g - AAm hydrogel. The biodegradability data is presented in Table 3.0.

Table 3.0 Biodegradability Study of Pectin and 7% grafted Pectin – g - AAm hydrogel

Sr. No.	Duration	Apple Pectin	Pectin – g - AAm hydrogel
1	24Hr	4%	2%
2	48Hr	10%	6%
3	72 Hr	24%	14%
4	96Hr	46%	36%
5	120Hr	64%	56%
6	144Hr	92%	76%
7	168Hr	100%	94%

From biodegradability data, it is clear that the Apple Pectin is highly biodegradable in comparison to the AAm grafted Hydrogel. This is because grafting leads to the stabilization and Insolubilization of the polymeric network and hence reduces the biodegradation process.

IV. CONCLUSION

The paper aims to synthesize the pectin and its grafted acrylamide-based hydrogel from waste apple pomace from a fruit processing plant in India. The synthesis of Pectin – g – AAm hydrogel was successfully optimized for different reaction parameters and it has been observed from studies carried out above that for pectin, the sorption of Co^{2+} ion is appreciable than Fe^{2+} followed by Cu^{2+} . The comparison of metal ion uptake on different grafting percent of Pectin – g – AAm hydrogel it follows that sorption of Cobalt is maximum followed by Iron and Copper ions. The sorption of grafted hydrogel is also higher than the parent polymer. The biodegradability study of pectin and Pectin – g – AAm hydrogel also supports the favourable degradation of both for pre - characterized soil.

The results opened the potential application areas for extracted Pectin and Pectin – g – AAm hydrogel in the removal of heavy metal ions from the waste industrial water and from heavy metal-contaminated water treatment. The use of Apple pomace for the extraction of pectin also emphasizes its application in green chemistry. The successful synthesis of hydrogels and biodegradability study opens the gates for the synthesis of pectin nanogels for use in various medical, pharmaceutical and commercial applications.

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