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Graft Copolymerization of Acrylamide on to Psyllium and Its Applications

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Abstract

Psyllium is among one of the most important and most studied polysaccharides. The graft copolymerization of acrylamide onto psyllium by microwave initiated synthesis without using any initiator. The different reaction parameters such as monomer concentration, polysaccharide concentration, reaction temperature, reaction time, pH were optimized to get the maximum percent grafting. The maximum percent grafting was observed at 97℃, 26×10^{-2} M/L of acrylamide and 60 second time of exposure. The formation of polymer was confirmed by FTIR, TGA, XRD and SEM spectroscopy. The graft copolymer has been successfully used for the removal of metal ions, organic dyes from aqueous system and decolouration of dye solution.

Keywords: Acrylamide,graft copolymerization, microwave irradiation, psyllium.

INTRODUCTION

These days modified polysaccharides have been the major area of scientific research. These polysaccharides being cost effective, biodegradable and quite efficient towards various technological processes, provides a better option for the artificial synthetic materials. Lot of work has been carried-out on various polysaccharides such as starch [1], cellulose [2], chitosan [3], dextrin [4], guar-gum [5], psyllium [6] and many more. The end products obtained were found to be the quality products as they were efficiently used in different technological processes viz. drug- delivery [7, 8], agriculture [9,10], water treatment [11] (removal of toxic metal ions from wastewater and flocculation) and membrane technology[12].Psyllium is mucilage forming natural polysaccharide, mainly known for its medicinal value. Chemically,psyllium husk is composed of arabinoxylan[13], which is complex polysaccharide having linearly joined β-1,4-linked D-xylopyranose units side branches of α-L-arabinofuranose residues [14].They found that themodified polymer was very efficient flocculent forthe removal of toxic effluents from sewage, tanneryand textile waste-water.The microwave irradiation is an efficient method, which results in rapid transfer of energy in the bulk of the reaction mixture. The microwave-initiated graft copolymerization requires a very short reaction time and proceeds even in the absence of any redox initiator [15]. In the present study psyllium has been modified through grafting with acrylamide with microwave initiated synthesis. The synthesized graft copolymer has been used for the removal of metals ions, dye adsorption, decolouration of dye solution.

Materials Used - Plantago psyllium, acrylamide,deionized water, acetone (Qualigen), methanol (Fisher scientific), ethanol (CDH), propanol (CDH), butanol (CDH), NaOH (CDH), Conc.HCl, benzene (AR), CCl_4 (AR), methylene blue (unaligned), $CuSO_4.5H_2O$(CDH), $NiSO_4.6H_2O$, (CDH), $MgSO_4.7H_2O$

(CDH).Weighing was done on electronic balance, Samsung GF83HT domestic microwave oven were used having power output (100-850W), FTIR- Fourier Transform infrared spectral analysis of the grafted sample were performed with Nicolet IF-10 spectrophotometer in the range 4000-400 by using KBr pallet, X-Ray Diffraction studies- XRD patterns of the grafted sample was studied using X-ray powder diffractometer using Cu K-alpha radiation source 2θ and 5-60°C temperature range, generate at 40 KV/30m, Thermo Gravimetric Analysis-TGA analysis of the pure psyllium and grafted sample was done using NETZSCH STA449F3A-0790-M instrument at a heating rate of 20K per 10 minute in nitrogen atmosphere and the weight losses at different stages were analyzed, SEM- Model JFM 5400, Jeol make has been used to obtain the micrograph of psyllium and psy-g-poly(acrylamide) graft copolymer sample.

Preparation of Polyacrylamide- Graft copolymerization of acrylamide on to psyllium was carried out using a solution of psylliun (4g/L), a known amount of acrylamide was added and the reaction mixture was irradiated in a domestic microwave oven in a flask, reaction was repeated in different monomer concentration in the range of (8.8×10^{-2} to 26×10^{-2} mole/liter), microwave power, exposure time, polysaccharide concentration, effect of time, temperature, pH. The average bulk temperature of the end of the reaction was measured by inserting thermometer in the reaction mixture. The reaction product was precipitated with DMF and wash with water for removal of unreact monomer. Dry the polymer in hot air oven (60°C) than wash again with the help of acetone (many times) than wash with DI water to remove attached homopolymer from grafted copolymer. The graft copolymer was than dried in a hot air oven at 60°C to a constant weight. Then finally weight the grafted copolymer, percent grafting and percent efficiency of the psyllium-g-poly(acrylamide) were calculated according to the formula [24]

$$\% G = \frac{W_1 - W_0}{W_0} \times 100$$

$$\% E = \frac{W_1 - W_0}{W_2} \times 100$$

Where W_1, W_0 and W_2 denoted the weight of the grafted psyllium, weight of original psyllium, weight of the monomer used respectively.

Result and discussion: -

To find out the optimum conditions for the grafting under microwave without adding any radical or catalyst, various reaction parameters were varied and the result were summarized. The maximum grafting of 132 and maximum efficiency 285 was obtained at optimized reaction time 60 second, MW power 850W, and monomer concentration 26×10^{-2} M/L and psyllium concentration is 4g/L and temperature is 97°C, total reaction volume fixed at 25 ml.

Monomer concentration: - Percent grafting was studied as a function of amount ofacrylamide and the result are presented in figure 1,maximum percent grafting 132 and efficiency 285 was obtained at 26×10^{-2} g/L of acrylamide and 4g/L psyllium taking other variables kept constant.

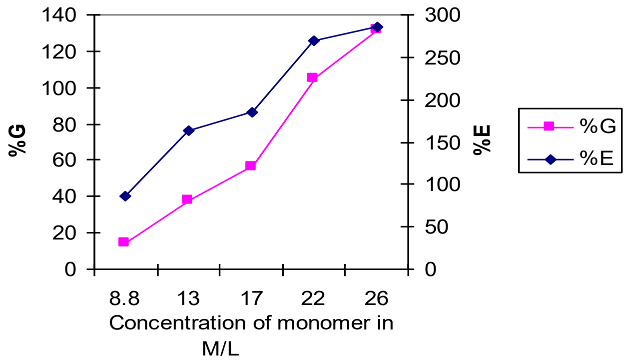

Figure 1:- %G and %E change with change in monomer concentration at fixed concentration of psyllium 4 g/l, exposure time 60, 850W microwave power,volume of solvent is 25 ml.

Effect of Temperature: - It is clear from the figure 2 that grafting yield increases with increases in temperature and reached to maximum value at 97℃ percent grafting was 132 and percent efficiency was 285.

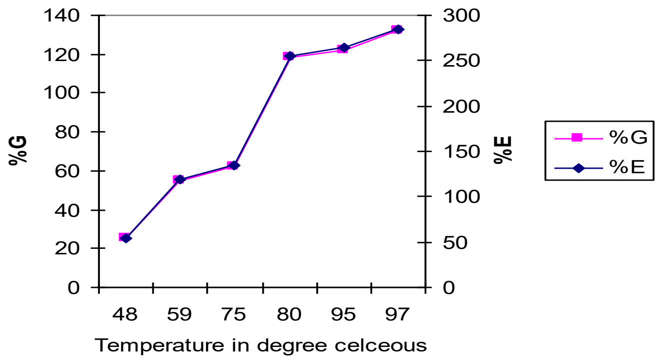

Figure 2:-% G and % E change with different temperature at fixed conc. of acrylamide 26×10^{-2} M/L , psyllium 4g/L, exposure time 60 sec. Volume of solvent is 25ml.

Effect of different solvent-In grafting mechanism, the solvent is the carrier by which monomer are transported to the vicinity of the back bone. The solubility of the monomer depends on the nature of the solvent and the polymer. Alcohols are useful solvents for grafting. This is because alcohols can swell the back bone effectively. This extent of grafting increases progressively when the alcohols is changed for methanol to butanol. Figure 3 showed that maximum % G and % E was found in the presence of butanol (% G is 66 and % E is 125%) this increases in grafting is due to the gradually increase swelling properties of the alcohols.

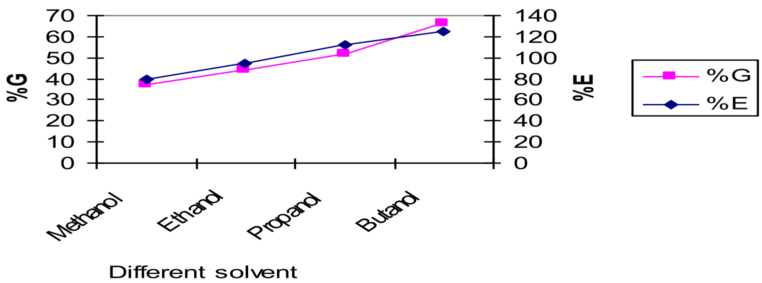

Figure 3:-% G and % E change with different alcohols at fixed concentrationof acrylamide 26×10^{-2} M/L, psyllium 4g/L, exposure time 60second, volume of solvent 25ml.

Effect of exposure time:-

Figure 4 representsthe effect of reaction time on percent grafting and efficiency, we observed from Figure 4 that percent grafting increases with increasing time of reaction giving maximum percent grafting 132 and percent efficiency 285 in 60 secondexposure at fixed concentration of monomer 26×10^{-2} M/L, psyllium 4g/L, 850 W microwave power, temperature is 97°C and total reaction volume fixed at 25 ml.

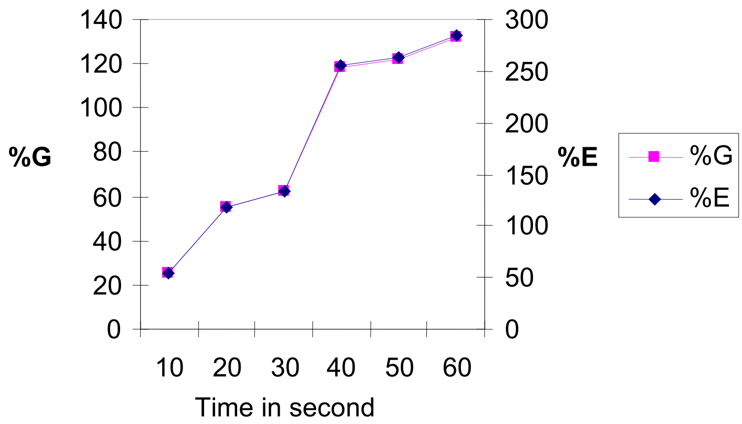

Figure 4:- %G and % E change with different mw power at fixed concentration of acrylamide 26×10^{-2} M/L, Psyllium 4g/L, exposure time is 60 second, volume of solvent is 25ml.

Effect of pH -Figure 5 showed the effect of pH on percent grafting and percent efficiency. Graft copolymerization was carried out in acidic (0.5N HCl), neutral (Deionizer water), and basic (0.5N NaOH) medium and maximum grafting (132%) was found in neutral medium, whereas in acidic (% G 5, % E 11) and basic medium (% G 31 ,% E 67) less grafting and less efficiency are found in acidic medium. This is due to the reason that H^+ ion of the active OH groups on the back bone chain got replaced with that of Na^+ and Cl^{-1}, thereby, decreasing the number of active sites present on the back bone chains and leading negligible percent grafting.

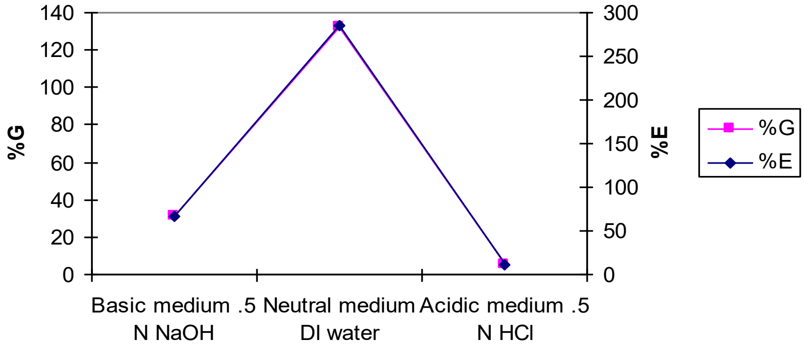

Figure 5:- % G and % E change with Acidic, basic and neutral medium at fixed conc. of monomer $26{\times}10^{-2}$ M/L and, psyllium (4g/L), and exposure time 60 second, 850W microwave power and volume of solvent 25ml.

Polysaccharides Concentration- % G and % E both change with change in the conc. of the psyllium in the range of 2-12 gram/liter at the fixed concentration of acrylamide $26{\times}10^{-2}$ M/L, 850W mw power after 60 second exposure time at 97°C temperature and reaction volume is 25 ml. maximum percent grafting 132 and percent efficiency 285 was found at 4 gram/liter concentration of psyllium than further increases concentration of psyllium both percent grafting and percent efficiency decrease, which may be due to the increase in the viscosity of the reaction medium causing hindrance of the normal reaction and also due to decrease in the monomer: polysaccharide ratio.

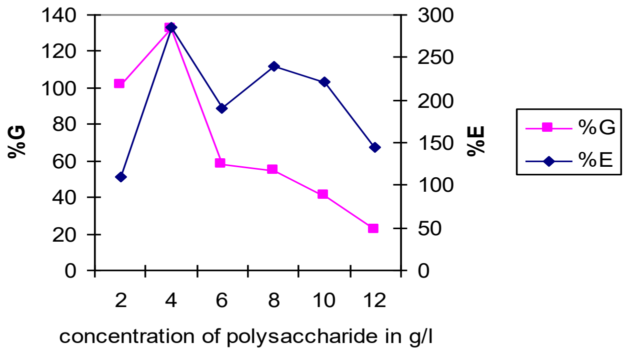

Figure 6:- % G and % E changed with polysaccharide concentration at fixed concentration of acrylamide $26{\times}10^{-2}$ M/L exposure time 60 second, 850 W microwave power and 25ml reaction volume.

Effect of Microwave Power:-On increasing microwave power from 180-850 W, grafting and efficiency increased (up to 850W Microwave power) at fixed conc. of acrylamide $26{\times}10^{-2}$ M/L, psyllium 4g/L, time 60 second. This may be due to the more availability of microwave power, causing more monomer and macro radicals and hence grafting.

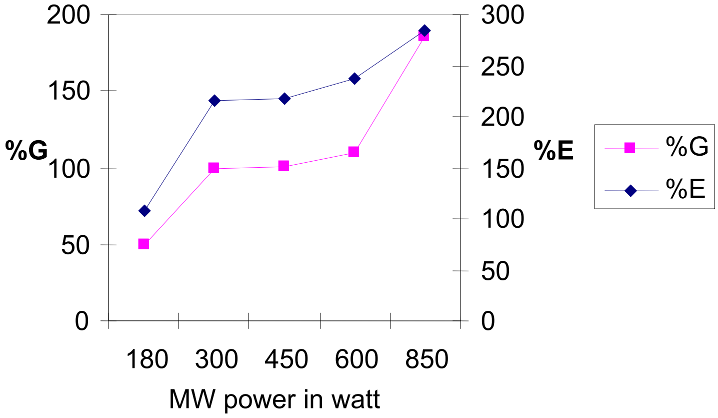

Figure 7:- % G and % E changed with mw power at fixed concentration of, acrylamide 26×10^{-2} M/L psyllium 4g/L, 70 second exposure and 25 ml reaction volume.

Overall maximum percent grafting and efficiency that could be achieved was 139% and 285% respectively at 26×10^{-2} M/L, 4 gram/L psyllium, 850 W microwave power ,60 second exposure keeping total reaction volume fixed at 25 ml.

Applications of graft copolymers-

Removal of metal ions- For the study Mg, Zn and Ni metals were taken. An important factor that affects the absorption of metal ions is the structure of the polymeric backbone. The synthesized psyllium-g-poly(acrylamide) removes metal ions. It is clear from table the metal ions uptake percentage of Mg was higher than for Zn and Ni. This can be attributed to the fact that the Mg ion has a lower atomic radius than other metal ions and consequently its adsorption by polymer is high. The sequence of metal ions sorption was as follows: Mg> Ni> Zn.

Table1:- Result of metal ion adsorption by psyllium-g-poly(acrylamide)

Sr. No.	% Adsorption	Metal ions
1.	10.29	Zn
2.	13.39	Ni
3.	15.58	Mg

Dye adsorption from water system: The result of dye adsorption of psyllium-g-poly (Acrylamide) is shown in table2 psyllium due to its high contents of hydroxyl and, carboxylic functional groupshas high affinity for many classes of dyes.

Table 2: Adsorption of dye by psyllium-g-poly(acrylamide)

Sr. No.	Dye in ml/L	Adsorption of dye (qe) mg/ml.
1.	50 m/L	25.25
2.	100 m/L	52.5

3.	150 m/L	72.5

Decolouration rate of water system- The result of decolouration rate of this polymer is shown in table3.

Table 3: Adsorption of dye by psyllium-g-poly (acrylamide)

Sr. No.	Dye in ml/L	Decolouration rate E(%)
1.	50 m/L	5.59
2.	100 m/L	21.3
3.	150 m/L	34

Conclusion

It can be concluded from the above discussion that the functionalized polymers i.e. Psy-g-poly(acrylamide) was found to be chemical resistance and showed swelling in different solvents. Hence, used in field in metal ions adsorption, dye removal and decolouration rate of dye solutions.

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