

## A Study: Graft Copolymerization of Methylmethacrylate onto Psyllium

Pallavi Jatav<sup>1</sup>, Dr. Nivedita Agarwal\*

Department of Chemistry, Govt. Girls' P.G. college, Rewa-486001, India

\*corresponding author

---

**Abstract:** The chemical modification of plantago psyllium, an anionic polysaccharide, was done by grafting of polymethylmethacrylate chains to prepare a graft copolymer (psy-g-MMA). It was synthesized under microwave irradiation without adding any radical or catalyst with 139% grafting using 850 W MW power in 70 second at MMA concentration 2 M/L, psyllium (10g/L). The maximum grafting was optimized by varying the MW power, exposure time and MMA/psyllium concentration. MW synthesized psy-g-PMMA copolymer was characterized by FTIR, TGA, XRD and SEM. The grafted sample was evaluated for physicochemical properties such as swelling behavior, chemical resistance. The graft copolymer has been successfully used for the removal of metal ions, dye adsorption and decoloration of dye solution.

**Key words** –graft copolymerization, methyl methacrylate(MMA), microwave irradiation, percent grafting (%G), percent efficiency (%E), psyllium.

---

### I. Introduction

Natural polymers, polysaccharides hold advantages over the synthetic materials mainly because they are nontoxic, cost effective, freely available, biodegradable and quite efficient towards various technological processes. In spite of enormous applications of polysaccharides a variety of chemical modification are employed to these carbohydrate polymers to explore their high potential. Grafting of vinyl monomers onto natural polymers is one of the most effective methods to improve the performance of natural polymers by enhancing their resistance towards chemicals, solvents and moisture, without sacrificing its biodegradable nature. Various polysaccharide graft copolymers have been reported [1-6]. 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] 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  $\beta$ -1,4-linked D-xylopyranose units side branches of  $\alpha$ -L-arabinofuranose residues[14]. Mishra et al. have found that the modified psyllium was very efficient flocculent for the removal of toxic effluents from sewage, tannery and textile waste-water.

Metals are absorbed at polymeric backbone mainly by secondary bonding interactions like hydrogen bonding; coordinate bonding of metal ions to the electron donating groups present at the polymer. In polysaccharides large number of –OH groups serves the metal ion coordination sites. By combining the metal ion attraction capabilities efficient low cost sorbents for the metal ions can be developed.

One of the best methods to synthesize graft copolymer is microwave irradiation either by microwave initiation method or microwave assisted method. In the present study poly methyl methacrylate –grafted psyllium were synthesised under microwave irradiation. The synthesis was done by varying reaction time, concentration of monomer and microwave power. The graft copolymer obtained was characterized on structural basis, thermal analysis and on morphological basis. An attempt was made to explore the utility of synthesized polymer for the removal of metals ions, dye adsorption, and decoloration of dye solution.

### II. Experimental

#### 2.1 Materials and Methods

Plantago psyllium, Methylmethacrylate (Acros chemicals), Acetone (Qualigen), Methanol (Fisher scientific), Ethanol (CDH), Propanol (CDH), Butanol (CDH), NaOH (CDH), Conc.HCl, Benzene (AR), CCl<sub>4</sub> (AR), methylene blue (unaligned), CuSO<sub>4</sub>.5H<sub>2</sub>O(CDH), NiSO<sub>4</sub>.6H<sub>2</sub>O, (CDH), MgSO<sub>4</sub>.7H<sub>2</sub>O (CDH) were used as received. Samsung GF83HT domestic microwave oven was used having power output (100-850W).

The synthesized graft copolymers were characterized with FTIR, SEM, TGA and XRD spectral analysis in order to know evidence of grafting. Fourier Transform infrared spectral analysis of pure psyllium and grafted psyllium were performed with Nicolet IF-10 spectrophotometer in the range 4000-400 by using KBr pellets. TGA were made on NETZSCH STA449F3A-0790-M instrument in the range of 20/10.0 (K/min)/1000 in nitrogen atmosphere.

X-ray study was carried out on X-ray powder diffractometer using Cu K- $\alpha$  radiation.

The surface morphology of psyllium and grafted sample were studied with the help of JEOL scanning electron micrograph.

## 2.2 Graft copolymerization

Graft copolymerization of Methyl methacrylate onto psyllium was carried out by irradiation of reaction mixture in a domestic microwave oven in a flask; reaction was repeated in different monomer concentration, microwave power, exposure time, polysaccharide concentration, effect of time, temperature, pH. The reaction product was precipitated with methanol and wash with water for removal of monomer. The polymer was dried in hot air oven (60°C) than washed again with the help of acetone (many times) followed by washing with DI water to remove attached homopolymer from grafted copolymer. The graft copolymer was then dried in a hot air oven at 60°C to a constant weight. The percent grafting (%G) and percent efficiency (%E) of the psyllium-g-copolymer were calculated using the formula [15]:

$$\% \text{ Grafting} = \frac{W_1 - W_0}{W_0} \times 100 \dots \dots (1)$$

$$\% \text{ Efficiency} = \frac{W_1 - W_0}{W_2} \times 100 \dots \dots (2)$$

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

## III. Physico- Chemical Behaviors Of Graft Copolymers

### 3.1 Swelling Behavior

A known amount of the sample was kept in solvent 24 hour. After the stipulate time, the graft copolymer was removed from the water and the extra liquid was removed by blotting with soft filter paper and then weighed. Percent swelling was determined as follows-

$$\% \text{ Swelling} = \frac{W_s - W_0}{W_0} \times 100 \dots \dots (3)$$

Where –  $W_s$ - weight of swollen sample and  $W_0$ - weight of original sample.

Swelling of sample was studied in water at different pH by keeping a known amount of sample for 6h and 24 h.

### 3.2 Chemical resistance

Chemical resistance of graft copolymers was studied as a function of percent weight loss by immersing the known amount of grafted sample in the solution of HCl and NaOH known concentration for 72 hours. The sample was then taken out and dried to constant weight in hot air oven. The percent weight loss was calculated by using the following expression:

$$\% \text{ Weight loss} = \frac{W_i - W_f}{W_i} \times 100 \dots \dots (4)$$

Where  $W_i$  is the initial weight of sample and  $W_f$  is the final weight of sample.

### 3.3 Removal of metal ions

In this study Mg, Zn and Ni metals are taken under investigation. Graft copolymer was used for removal of metal ions from water system. Adsorption was carried out by stirring 0.1 gram of grafted polymer for 30 minutes in 25 ml solution containing ions (Ni, Zn, Mg), after filtration, the remaining metal ions in the filtrate were determined.

$$\% \text{ Adsorption} = \frac{C_0 - C_e}{C_0} \times 100 \dots \dots (5)$$

Where  $C_0$  is initial concentration of metal ion,  $C_e$  is remaining metal ion in filtrate

### 3.4 Dye adsorption behavior

The graft copolymers were used for dye adsorption behavior. The known weight of grafted sample was put into the solution of different concentration of methylene blue for 3 hours. Then after filtration dry the grafted polymer, weight it.

$$\text{Dye Adsorption (qe)} = \frac{C_0 - C_e}{W} \times V \dots \dots (6)$$

Where  $C_0$  is the initial concentration,  $C_e$  is the adsorption of sample,  $V$  is volume,  $W$  is the weight of grafting sample.

### 3.5 Decoloration rate of Dye solution

The known amount of grafted sample was put into the solution of different concentration of methylene blue for 3 hours, than after and before filtration the absorbance of the filtrate was determined at 660nm- 680nm using spectrophotometer.

$$\text{Decoloration rate (E)} = \frac{A_0 - A}{A_0} \times 100 \dots \dots (7)$$

Where  $A_0$  and  $A$  absorbance of dye solution before and after treatment.

## IV. 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 139% was obtained at optimized reaction time 70 second, MW power 850W, and monomer concentration 2 M/L and psyllium concentration is 10g/L and temperature is 97°C.

### 4.1 Monomer concentration

Percent grafting increased with increasing monomer concentration, however efficiency decrease under the fixed concentration of psyllium 10g/L, 850 W microwave power and 70 second exposure in 25ml reaction volume (fig.1). The increase in percent grafting may be due to the generated of more grafting sites and also availability of extra monomer for grafting. Decrease in efficiency on increasing the monomer concentration, may be probably due to more homopolymer formation.

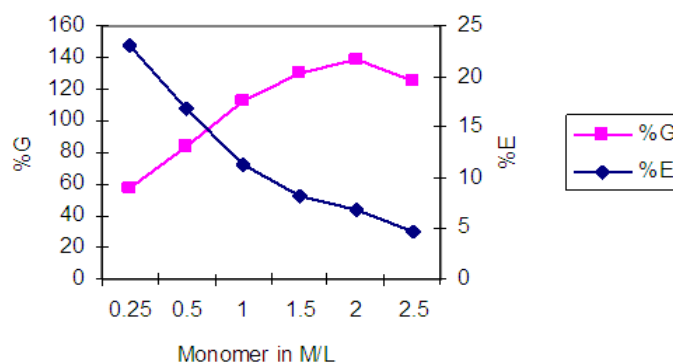


Figure 1:- % G and % E change with different concentration of monomers at fixed concentration of psyllium 10g/L, exposure time 70 second, MW power 850W, and volume of solvent is 25ml.

### 4.2 Effect of Temperature

It is clear from the figure 2 that grafting yield increases with increases in temperature and reached to maximum value 139 % grafting and 6.87 percent efficiency at 97°C.

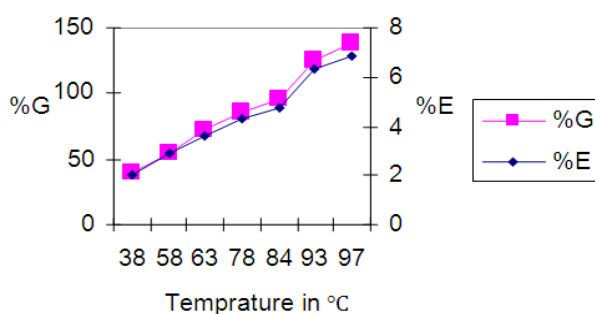


Figure 2:- % G and % E change with different temperature at fixed conc. of MMA (2M/L), psyllium 10g/L, exposure time 70 second, MW power 850W, Volume of solvent is 25ml.

### 4.3 Effect of 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 grafting decrease progressively higher members of alcohols, (Fig.3) maximum percent grafting and percent efficiency was found in the presence of methanol, percent grafting is 56 and percent efficiency is 2.7.

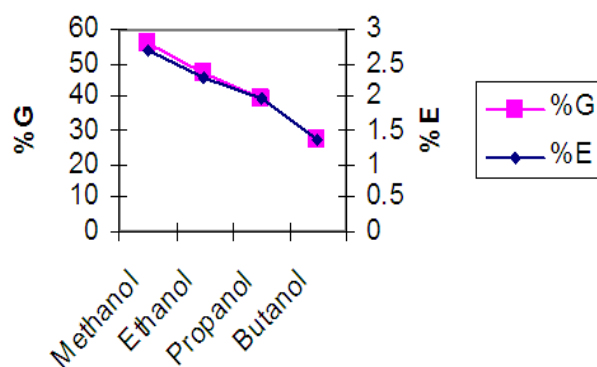


Figure 3:- % G and % E change with different alcohols at fixed concentration of MMA (2M/L), psyllium 10g/L, exposure time 70sec. , volume of solvent 25ml.

### 4.4 Effect of exposure time

Grafting increased with increases in exposure time 10 to 70second at fixed concentration of MMA (2M/L). Psyllium 10g/L, MW power (850W), reaction volume (25ml). The % grafting and the % efficiency were observed to increase on increasing the exposure time (Fig.4). This is may be due to the availability of more microwave energy resulting into extra radicals for the graft copolymerization.

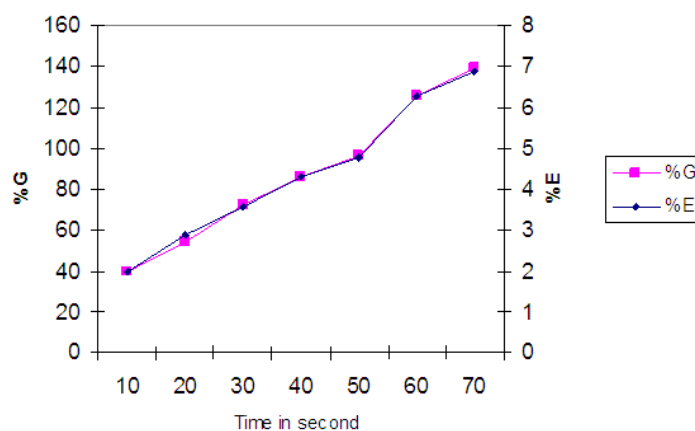


Figure 4: %G and % E change with different mw power at fixed concentration of MMA (2M/L, Psyllium10 g/L, exposure time is 70 second, volume of solvent is 25ml.

### 4.5 Effect of pH

Figure5 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 139 was found in neutral medium. Whereas acidic (percent grafting 12 percent efficiency 0.599) and basic medium (percent grafting 80.8, percent efficiency 4) were observed, 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  $Cl^-$  respectively thereby, decreasing the number of active sites present on the back bone chains and leading negligible grafting and efficiency.

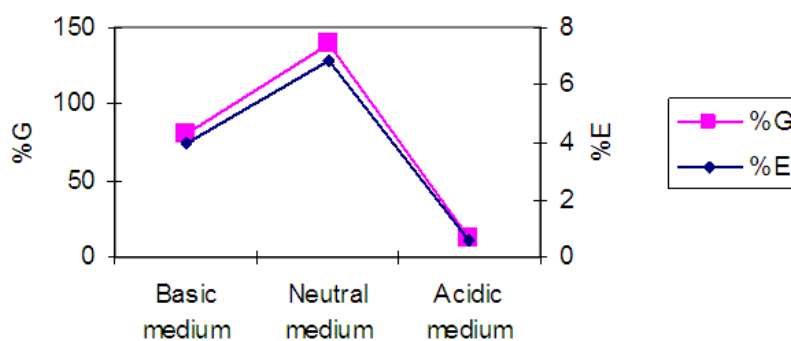


Figure 5:- % G and % E change with Acidic, basic and neutral medium at fixed conc. of MMA(2M/l), Psyllium (10g/L), and exposure time 70 sec. volume of solvent 25ml.

#### 4.6 Polysaccharides Concentration

% G and % E both change with change in the concentration of the psyllium in the range of (0.15 to 0.35 gram/ 25ml) at the fixed concentration of the MMA 2M/L at 850W mw power after 70 sec exposure time at 97°C temperature and reaction volume is 25 ml, maximum % G (132%) and %E (285%) was found at 10g/L concentration of psyllium (fig. 6) than further increases concentration of psyllium both % G and % E 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.

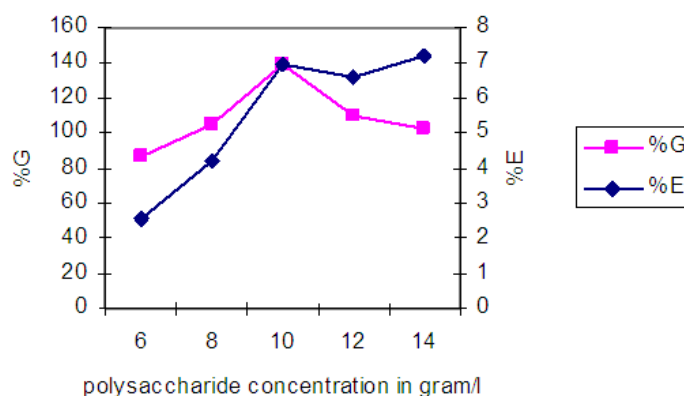


Figure 6:- % G and % E with changing polymer conc.at fixed concentration of MMA 2M/ exposure time 70 sec.

#### 4.7 Effect of Microwave Power

On increasing microwave power from 180-850 W, grafting and efficiency increased (up to 850 W microwave power) at fixed conc. of MMA 2M/L ,Psyllium 10g/L. Time 70 second. This may be due to the formation of more radicals for graft copolymerization in high microwave power.

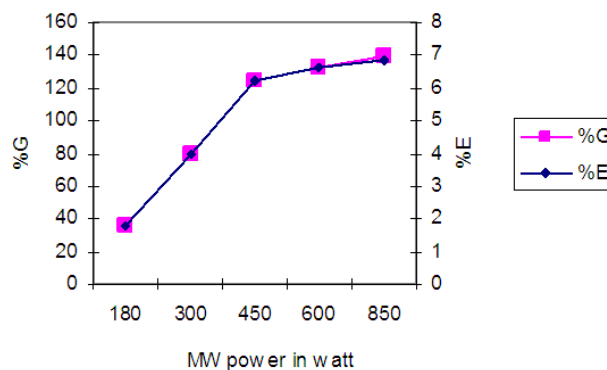


Figure 7:- % G and % E with changing mw power at fixed concentration of MMA 2M/L, psyllium 10 g/L, exposure time, and 70sec.

#### 4.8 Physico-chemical properties-

##### 4.8.1 Swelling behavior

The Swelling studies of psyllium poly(MMA) were carried out in different solvents as shown in Table1. The maximum swelling was observed for psyllium-g-poly (MMA) in water is 2476. This may be due to possible porosity of particles originated due to grafting of MMA on to psyllium The psyllium-g-poly(MMA) shows the following swelling behavior in different solvents Water > n-butanol > CCl<sub>4</sub> > Benzene .

**Table 1:- Swelling behavior of psy-g-poly(MMA) in different solvents.**

Solvent	Initial weight of sample in gram	final weight of sample in gram	Swelling
Water	0.1 gram	2.576 gram	2476
CCl <sub>4</sub>	0.1 gram	0.136 gram	36
Benzene	0.1 gram	0.126 gram	26
n-butanol	0.1 gram	0.165 gram	65

4.8.2 Evaluation of chemical resistance- It has been resulted that chemical resistance of psyllium-g-poly (MMA) polymer was more than psyllium itself (Table2).

**Table 2:- Percent weight loss shown by psyllium-g-poly (MMA) sample in HCl and NaOH.**

	Initial weight (gram)	final weight in 1N HCl	% weight loss	Final weight in 1N NaOH	% weight loss
Psyllium	0.1 gram	0.004 g	96	0.056	44
psyllium-g-poly(MMA)	0.1 gram	0.006 g	94	0.058	42

##### 4.8.3 Swelling at different pH

The swelling behavior at different pH was carried out in different pH solution (pH 4,7,9) at 37°C . The results summarized in table 3 show maximum % swelling at pH 9.

**Table 3:- Swelling behavior of psy-g-poly(MMA) in different pH solvents.**

Swelling time	Initial wt. of sample in gram	Final wt. of sample			% Swelling of sample		
		pH 4	pH 7	pH 9	pH 4	pH 7	pH 9
6 Hour	0.1gram	0.940	0.980	1.110	840	880	1010
24 Hours	0.1gram	1.389	1.486	1.850	1289	1386	1750

##### 4.8.4 Removal of metal ions

In this study Mg, Zn and Ni metals are taken under investigation. Structural aspects of the polymeric back bone are important factors affecting metal ions sorption. The synthesized psyllium-g-poly(MMA) removes metal ions. Metal ions are removed by chelating with amide functional groups present in the graft copolymer. It is clear from table 4, 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.

**Table 4:- Result of metal ion adsorption by psyllium-g-poly (MMA).**

Sr. No.	% Adsorption	Metal ions
1.	8.62	Zn
2.	11.56	Ni
3.	12.98	Mg

##### 4.8.5 Dye adsorption from water system

The result of dye adsorption of psyllium-g-poly(MMA) is shown in Table5. Psyllium due to its high contents of hydroxyl and, carboxylic functional groups, has high affinity for many classes of dyes.

**Table 5:- Adsorption of dye by psyllium-g-poly (MMA)**

Sr. No.	Dye in ml/L	Adsorption of dye (qe) mg/ml.
1.	50 ml/L	5.25
2.	100 ml/L	22.5
3.	150 ml/L	52.2

#### 4.8.6 Decoloration rate of water system

The result of decoloration rate of dye solution by psyllium-g-poly(MMA) is shown in Table 6. The carboxylic and hydroxyl group on psyllium-g-poly(MMA) are responsible for decoloration of methylene blue dye solution. It is evident that decoloration of methylene blue on to grafted psyllium was rapid at lower concentration and their after it proceeds at a slower rate.

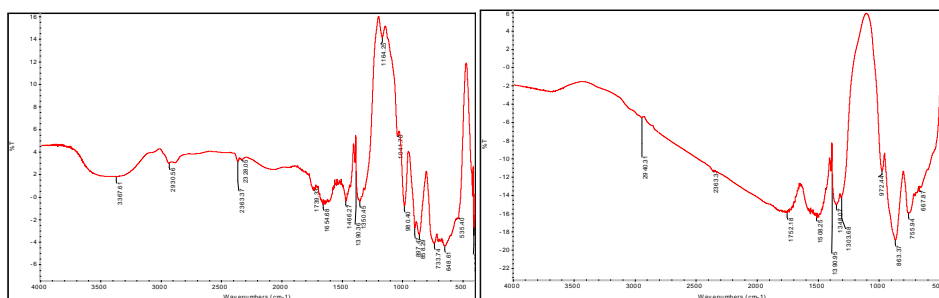
**Table 6:- Decoloration of dye by psyllium-g-poly (MMA)**

S.no.	Dye in ml/L	Decoloration rate E(%)
1.	50 ml/L	17.75
2.	100 ml/L	30.8
3.	150 ml/L	34

#### 4.9 Characterization-

##### 4.9.1 FTIR

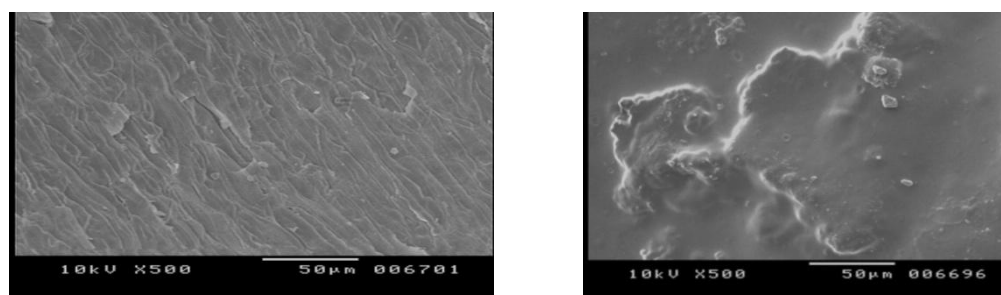
Spectral analysis was used to confirm the graft copolymerization reaction. FTIR of pure psyllium (Figure 8(a)) shows peak at  $3367.61\text{ cm}^{-1}$  due to OH stretching absorption, band at  $2926.7\text{ cm}^{-1}$  is observed due to -OH and CH asymmetric stretching vibration; band at  $1466.27\text{ cm}^{-1}$  is observed due to C-H deformation vibration. The most prominent peak  $1164.25\text{ cm}^{-1}$  is due to  $\text{-C=O}$  of COOH group and C-O-C stretching vibrations. Peak at  $533\text{ cm}^{-1}$  and  $857\text{ cm}^{-1}$  is due to pyranose ring. The FTIR spectrum of psyllium-g-poly(methylmethacrylate) Figure 8(b) shows an additional band at  $1348.08\text{ cm}^{-1}$  due to C-H bending. Earlier peaks at  $535.40\text{ cm}^{-1}$ ,  $972.37\text{ cm}^{-1}$ , and  $1752.18\text{ cm}^{-1}$  after grafting are observed at  $667.87\text{ cm}^{-1}$ ,  $980.40\text{ cm}^{-1}$ ,  $1752.18\text{ cm}^{-1}$  respectively. An additional peak observed at  $1752.18\text{ cm}^{-1}$  refers to the (C=O) group in MMA.



**Figure 8:- (a) FTIR of pure psyllium. (b) FTIR of psy-g-poly(MMA).**

##### 4.9.2 SEM

Scanning electron micrographs of pure psyllium and grafted psyllium with methylmethacrylate reveals a clear cut distinction between the grafted and ungrafted psyllium, pure psyllium has fibrous elongated structure with smooth surface whereas psyllium-g- methylmethacrylate has cloudy structure with uneven surface.



**Figure 9: (a) SEM of psyllium. (b) psyllium-g-poly(MMA).**

##### 4.9.3 TGA

TGA studies of both the back bone (Figure 10b) and functionalized polymer (Figure 10a) were performed as a function of percent weight loss vs. temperature. It has been found that in case of psyllium, initial decomposition temperature (IDT) due to dehydration were observed at  $246.9^{\circ}\text{C}$  with 10.73 % weight loss is higher as compared to that of psy-g-poly(MMA)  $241.4^{\circ}\text{C}$  with 13.2 % weight loss in nitrogen atmosphere. This appears due to initial disturbance in the crystalline structure of the backbone during graft copolymerization. Whereas final decomposition temperature (FDT) of psy-g-poly(MMA) is  $322.3^{\circ}\text{C}$  with 58.04% weight loss is slightly higher than psyllium  $321.4^{\circ}\text{C}$  with 53.55% weight loss which shows more thermal stable as compared to psyllium and in initial decomposition stage psyllium is thermally more stable as compared to psy-g-poly(MMA).



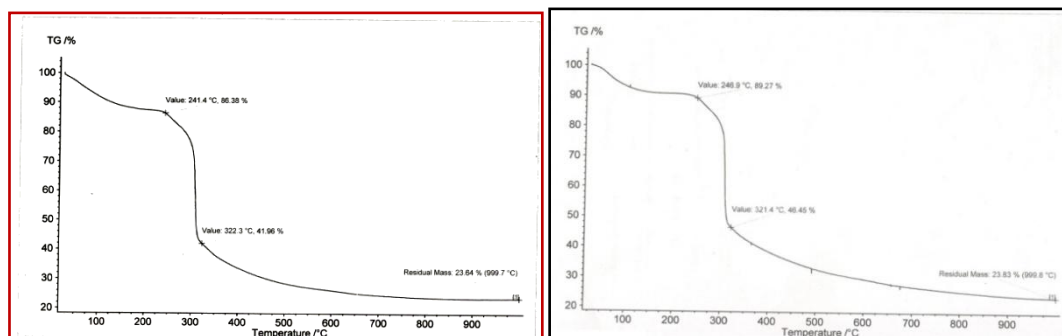


Figure 10: (a) TGA of psy-g-poly(MMA). (b) TGA of pure psyllium.

#### 4.9.4 X-ray diffraction analysis

XRD spectrum of both psyllium and psy-g-poly(MMA) showed in figure 11.a and Figure 11.b respectively we observed that XRD of pure psyllium showed in amorphous region and grafted psyllium also show amorphicity, on studying both XRD spectra we concluded that the diffraction peak intensity of pure psyllium are not significantly reduced after grafting at all angle but the XRD of grafted spectrum present in saltily broad spectrum as compared to pure psyllium means slightly increase the amorphous nature of crystals because of small amount of disturbance in the crystal lattice of raw materials means psyllium this type of results found may be due to incorporation of polymethylmethacrylate chains onto the active sites of the polymers back bone(psyllium) during grafting, which there by results in little morphological transformation and a slightly increase in amorphc nature and crystallinity of grafted polymers.

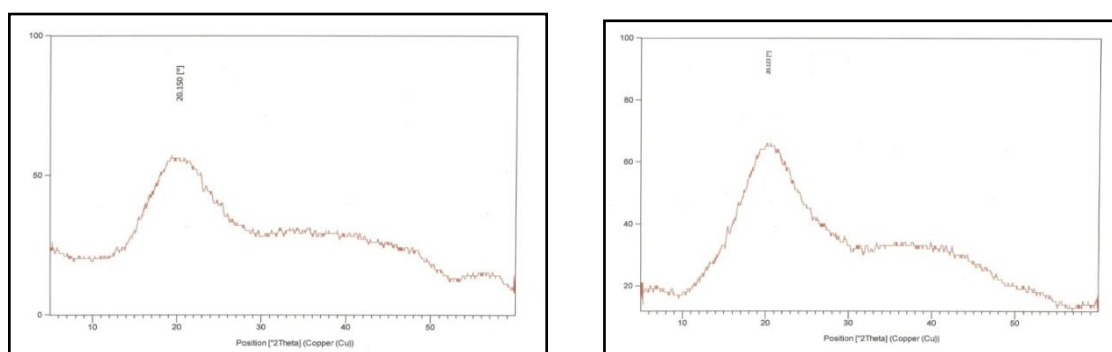


Figure 11: (a) XRD of psy-g-poly(MMA). (b) XRD of pure psyllium.

## V. Conclusions

Based on the results presented in this paper. We concluded that psyllium-grafted-poly(methylmathacrylate) were successfully synthesized without using any catalyst or initiator in domestic microwave oven , the proof of grafting was obtained from FTIR, SEM, TGA, AND XRD analysis. synthesized copolymer were used as metal ion adsorbents, dye removal and decoloration of dye solution, This type of work could encourage the synthesis of new graft copolymers in very short reaction time.

**Acknowledgement-**The authors are grateful to UGC, for financial support for the study.

## References

- [1]. Lee J.S., Kumar R.N., Rozman H.D., Azemi M.N.: Pasting, swelling and solubility properties of UV initiated starch-graft-poly(AA). Food Chemistry, **91**, 2-03–211 (2005).
- [2]. Kumar V., Bhardwaj Y.K., Rawat K.P., Sabharwal S.: Radiation-induced grafting of vinylbenzyltrimethylammonium chloride (VBT) onto cotton fabric and study of its anti-bacterial activities. Radiation Physics and Chemistry, **73**, 175–182 (2005).
- [3]. Singh V., Tripathi D.N., Tiwari A., Sanghi R.: Microwave synthesized chitosan-graft-poly(methylmethacrylate):An efficient Zn<sup>2+</sup> ion binder. Carbohydrate Polymers, **65**, 35–41 (2006).
- [4]. E. Cohen, A. Zilkha: Anionic graft polymerization of methyl methacrylate on starch and dextrin. Journal of Polymer Science Part A-1: Polymer Chemistry, **7**, 1881–1892 (2003).
- [5]. P.K. Pandey, A. Srivastava, J. Tripathy, K. Behari: Graft copolymerization of acrylic acid onto guar gum initiated by vanadium (V)-mercaptosuccinic acid redox pair. Carbohydrate Polymers, **65**, 414–420(2006).
- [6]. Mishra A., Bajpai M. : Flocculation behaviour of model textile wastewater treated with a food grade polysaccharide. Journal of Hazardous Materials, **118**, 213–217 (2005).
- [7]. Kang G.D., Cheon S.H., Song S.C.: Controlled release of doxorubicin from thermo sensitive poly(organophosphazene) hydrogels. International Journal of Pharmaceutics, **319**, 29–36 (2006).



- [8]. Kang G.D., Cheon S.H., Khang G., Song S.C.: Thermosensitive poly(organophosphazene) hydrogels for a controlled drug delivery European Journal of Pharmaceutics and Biopharmaceutics, **63**,340–346 (2006).
- [9]. Rudzinski W.E., Dave A.M., Vaishnav U.H., Kumbar S.G., Kulkarni A.R., Aminabhavi T.M.: Hydrogels as controlled release devices in agriculture. Designed Monomers and Polymers, **5**, 39–65 (2002).
- [10]. Rudzinski W.E., Chipuk T., Dave A.M., Kumbar S.G., Aminabhavi T.M.: pH-sensitive acrylic-based copolymeric hydrogels for the controlled release of a pesticide and a micronutrient. Journal of Applied Polymer Science, **87**, 394–403 (2002).
- [11]. Okieimen F.E., Sogbaike C.E., Ebhoaye J.E.: Removal of cadmium and copper ions from aqueous solution with cellulose graft copolymers. Separation and Purification Technology, **44**, 85–89 (2005).
- [12]. Huang J., Wang X.L., Yu X.H.: Solute permeation through the polyurethane-NIPAAm hydrogel membranes with various cross linking densities. Desalination, **192**, 125–131 (2006).
- [13]. Fischer M.H., Yu N., Gray G.R., Ralph J., Anderson L., Marlett J.A.: The gel-forming polysaccharide of psyllium husk (*Plantago ovata* Forsk). Carbohydrate Research, **339**, 2009–2017 (2004).
- [14]. Izydorczyk M.S., Biliaderis C.G.: Cereal arabinoxylans: Advances in structure and physicochemical properties J. Carbohydrate Polymers, **28**, 33–48. (1995).
- [15]. Singh R.V., Poly(acrylonitrile) grafted Cassia pudibunda seed gum: a potential commercial gum from renewable source, Journal of Applied polymer Science, **99**,619-627(2006).