Microwave assisted synthesis of poly(2-hydroxyethylmethacrylate) grafted agar (Ag-g-P(HEMA)) and its application as a flocculant for wastewater treatment

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Abstract Poly(2-hydroxyethylmethacrylate) chains were grafted onto the backbone of agar using a microwave assisted method involving a combination of microwave irradiation and ceric ammonium nitrate to initiate the grafting reaction. The synthesized graft copolymers were characterized by intrinsic viscosity measurements, Fourier transform infrared spectroscopy, elemental analysis (C, H, N, O and S) and scanning electron microscopy. Ag-g-P (HEMA)-2 showed a much higher flocculation efficacy than agar. The optimized dosage of flocculation for Ag-g-P (HEMA)-2 in the wastewater was found to be 0.75 ppm. Compared to agar, Ag-g-P(HEMA)-2 was found to considerably reduce the pollutant load in the wastewater.

Keywords agar, flocculant, microwave assisted synthesis, jar test protocol, poly(HEMA) grafted agar, wastewater treatment

1 Introduction

Agar $(C_{12}H_{18}O_9)_n$ is a biopolymer commercially obtained from *Gelidium* and *Gracilariae*, which belongs to the Rhodophyceae class of algae commonly known as red seaweed. Chemically, agar is a mixture of agarose and agaropectin. Agarose is a linear polymer, consisting of (1-3)- β -D-galactopyranose-(1-4)-3,6-anhydro- α -L-galactopyranose units. Agaropectin on the other hand is a heterogeneous mixture of smaller molecules. Agaropectin structure is similar to agarose structure but it is slightly branched, sulfated and it may have methyl and pyruvic acid ketal substituents. The presently accepted structure of agar [1,2] is depicted in Fig. 1.

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Fig. 1 Chemical structure of agar repeating unit $(n \sim 390)$

Agar was the first phycocolloid (gelatinous substance produced by red brown algae) to be used in the human food industry owing to its gelling characteristics. It is the only phycocolloid with this property. It is also used as a culture medium, a viscosifier in chromatographic techniques, a thickening agent and a mild laxative [3].

Graft copolymers are special types of branched copolymers consisting of a long backbone made up of repeating units (backbone polymer) with branches that are made up of other (chemically different) repeating units [4,5]. Graft copolymers can have desirable properties that are not inherent to the parent backbone. Since grafting is generally related to the side chains, it does not affect the backbone polymer, and so grafting only causes a little perturbation in the molecular properties of the backbone [6].

Grafting copolymerization occurs via a free radical addition copolymerization process. When an external agent (i.e., a chemical free radical initiator) is used to create the free radical sites on a polymer, the agent needs to only create the required free radical sites on the polymer chain and not damage the chain's structural integrity. The major methods to synthesize graft copolymers involve using a chemical free radical initiator, high energy radiation (gamma rays or electron beam), UV- radiation or microwave-based methods.

The conventional method of synthesis uses a chemical free radical initiator (e.g., ceric ammonium nitrate (CAN),

ceric ammonium sulphate (CAS), or Fenton's reagent) [7–12] to generate free radical sites on the polymer backbone, where the graft monomer is then attached to the parent chain to form graft chains. This method of synthesis has low reproducibility compared to the other techniques and is not very suitable for commercial scale synthesis.

The high-energy radiation [13–20] initiated method (gamma rays or electron beam) is not suitable for the synthesis of graft copolymers due to the high probability of damage to the polysaccharide backbone (radiolysis) owing to the high penetrating power of the radiation. UV radiation in the presence of a suitable photosensitizer [21–28] can also be used to initiate grafting; however, the low penetration power of the UV-rays restricts this method to surface grafting.

Microwave radiation is electromagnetic radiation. In the presence of microwave radiation selective excitation of polar bonds takes place. This results in rupture or cleavage at points of exposure and thus leads to the formation of free radical sites. Since the "C–C" backbone of the polymer is relatively nonpolar, it remains unaffected by the microwave radiation.

Recently, the field of graft copolymer synthesis has been revolutionized by using microwave radiation to generate free radical sites on the backbone polymer. Unlike conventional methods of synthesis, an inert atmospheric condition is not required in microwave based methods. These grafting methods are fast, easy to operate, highly reproducible and thus have all the qualities desired in a synthetic method.

Microwave-based graft copolymer synthetic methods have been classified into two types: 1) Microwave initiated synthesis. This technique employs only microwave radiation to create free radical sites on the polysaccharide, where the graft chains are then attached [29–35]. 2) Microwave assisted synthesis. This technique uses a combination of a chemical free radical initiator and microwave radiation to create free radical sites on the polysaccharide backbone, where the graft chains then grow [36–39].

Synthesized graft copolymers have been effectively used as flocculants for waste water treatment [10,32–34,36–39], matrixes for controlled drug release [31,35], viscosifiers, chelating agents [6], bioadhesives and drag reducing agents [40].

Flocculants are effective in separating colloidal particles, when added in small amounts (ppm level). The process of forming larger agglomerates of colloidal particles, aided by a polymeric material is called flocculation. No substantial changes in surface charges occur in flocculation. Agglomerates are formed by flocculation when the flocs are of large size, strongly bound and porous [41]. The flocculants can be natural (e.g., polysaccharides) or synthetic (e.g., polyacrylamide grafted polysacchar-

ides). Natural flocculants need to be used in large dosages due to their relatively low molecular weights and short shelf lives. However, they are economical; completely safe (non toxic) and form flocs with high shear stabilities. On the other hand, synthetic flocculants are effective in minute dosages and have longer shelf lives, but they form fragile flocs. By grafting polysaccharides with synthetic polymers, tailor-made materials with the advantages of both groups can be synthesized.

Graft copolymers are a special class of chelating polymers that have a modified backbone which binds metal ions by coordination or ionic interactions. The most common coordinating atoms present in the main chain or in the side chain are N, O, P, and S. Thus it is possible to make chelating polymers that have a selective absorption capacity for a specific metal ion by fixing the desired ligand groups on the polymer backbone [6]. Practically, chelating polymers are very useful for the selective absorption and recovery of metal ions from solutions.

In the present investigation, 2-hydroxyethyl methacry-late (HEMA) chains have been grafted on the backbone of agar, to form a "P(HEMA) grafted agar" (Ag-g-P (HEMA)). The synthesis was carried out by a microwave assisted method, using ceric ammonium nitrate (CAN) as the free radical initiator and microwave radiation (800 W). The intrinsic viscosity and the flocculation efficacy of the grafted product were measured and the application of the grafted product as a flocculant for wastewater treatment and pollutant load reduction was investigated.

2 Materials and methods

2.1 Materials

Agar was supplied by CDH, New Delhi, India and 2-hydroxyethylmethacrylate (the monomer) was from E. Merck, Germany. Ceric ammonium nitrate was supplied by E. Merck (India), Mumbai, India. Acetone was purchased from Rankem, New Delhi, India and hydroquinone was purchased from S. D. Fine Chemicals, Mumbai, India. All the chemicals were used as received, without further purification.

The wastewater was collected from the main sewage system of Birla Institute of Technology, Mesra (BIT-Mesra) community.

2.2 Synthesis

One gram of agar was dissolved in 40 mL of distilled water. The desired amount of HEMA was added to the agar solution and a catalytic amount of ceric ammonium nitrate (CAN) was also added. The solution was mixed well and transferred to 250-mL Borosil beaker. The beaker was

subsequently placed on the turntable of the microwave oven and the mixture was exposed to microwave irradiation (800 W). The microwave irradiation was temporarily paused when the reaction mixture started to boil ($\sim 65^{\circ}$ C). The mixture was then cooled by placing the beaker in ice cold water.

This microwave irradiation-cooling cycle was repeated until a gel like mass was formed or if no gelling took place, until the sample had been irradiated for a total of 3 min. After this, the beaker and its contents were cooled and kept undisturbed to complete the grafting reaction. Later, the gel-like mass in the beaker was poured into an excess of acetone. All impurities like the catalyst (ceric ion) and the homopolymers were removed by the acetone. The resulting jelly like precipitate of the graft copolymer was collected and dried in a hot air oven. Subsequently, the product was pulverized, sieved and purified by solvent extraction using a methanol-water mixture (50 : 50 by volume). The extraction removed any occluded HEMA that is formed by the competing homopolymer formation reaction. The percent grafting of the Ag-g-P(HEMA) synthesized by this microwave assisted method was calculated from the equation:

Grafting(%)

$$= \frac{\text{Wt of graft copolymer } - \text{ Wt of polyaccharide}}{\text{Wt of polyaccharide}}$$

$$\times 100\%. \tag{1}$$

2.3 Characterization

2.3.1 Intrinsic viscosity measurement

The viscosities of the various polymer solutions were measured with an Ubbelodhe viscometer (Constant: 0.003899) at 25°C in an aqueous medium. The pH of the solution was kept neutral. The flow times of the polymer solutions were measured at four different concentrations. The polymer solution flow time (t) and that of the solvent (t0, for distilled water) were used to calculate a relative viscosity, $\eta_{\rm rel} = t/t_0$. The specific viscosity was calculated from the relationship $\eta_{\rm sp} = \eta_{\rm rel} - 1$. Subsequently, the reduced viscosity ($\eta_{\rm sp}/C$) and the inherent viscosity ($\ln \eta_{\rm rel}/C$) were calculated, where "C" is the polymer concentration in g/dL. The intrinsic viscosity was obtained from the point of intersection after extrapolation of the two plots, i.e., $\eta_{\rm sp}/C$ versus C and $\ln \eta_{\rm rel}/C$ versus C, to zero concentration.

2.3.2 Elemental analysis

The elemental analyses of the agar and Ag-g-P(HEMA)-2 (optimum grade) were determined with an Elemental

Analyzer (Make-M/s Elementar, Germany; Model-Vario EL III). Five elements, carbon, hydrogen, nitrogen, oxygen and sulfur were determined.

2.3.3 Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra of the agar and Ag-g-P(HEMA)-2 were recorded by the KBr pellet method using a FTIR spectro-photometer (Model IR-Prestige 21, Shimadzu Corporation, Japan) between 400 and 4000 cm⁻¹.

2.3.4 Scanning electron microscopy

The surface morphology of the agar and Ag-g-P(HEMA)-2 were analyzed by scanning electron microscopy (SEM) (Model: JSM-6390LV, Jeol, Japan, equipped with an energy dispersive X-ray (EDX) analyzer with an accelerating voltage of 30 kV in the high vacuum mode). The surface of the samples was coated with a thin layer of platinum with a platinum coater (JEOL Auto fine coater model: JFC – 1600 auto fine coater, coating time: 120 s at 20 mA). The micrographs of these samples were recorded at various magnifications.

2.3.5 Flocculation studies

2.3.5.1 Flocculation study in a kaolin suspension

The flocculation efficacies of the various synthesized grades of Ag-g-P(HEMA) and the agar were studied using a standard "jar test" procedure in a 0.25% kaolin suspension. The jar test apparatus was from Simeco, Kolkata, India. The test protocol involved using a measured quantity (800 mL) of the 0.25% kaolin suspension in a 1000-mL Borosil beaker. The desired amount (0-1 ppm) of flocculant (the agar or the various grades of Agg-P(HEMA) was added to the kaolin suspension. No flocculant was added to the blank. The solutions were stirred by the jar test apparatus, at 150 r·min⁻¹ for 30 s or at $60 \,\mathrm{r \cdot min^{-1}}$ for 5 min, followed by 15 min of settling time. Afterwards, the supernatant liquid was collected and the turbidity was measured with a calibrated nephelo-turbidity meter (Digital Nephelo-Turbidity Meter 132, Systronics, India).

2.3.5.2 Flocculation study in wastewater

The flocculation efficacies of Ag-g-P(HEMA)-2 (the best grade) and the agar were studied in wastewater (using the "jar test" procedure as in Section 2.3.5.1). In addition, the reduction in the waste water pollutant load using the best grade of Ag-g-P(HEMA) as a flocculant was evaluated by comparing the parameters of the supernatant taken from three samples as follows. SET 1: Wastewater without flocculant; SET 2: Wastewater with 0.75 ppm of agar; SET

3: Wastewater with 0.75 ppm of Ag-g-P(HEMA)-2. The water quality of these supernatant solutions was analyzed by the standard procedures described below.

2.3.5.3 Chemical analysis of the supernatant solutions

The supernatant solutions described above were subjected to the following chemical analysis: (I) Turbidity was measured using a calibrated nephelo-turbidity meter (Digital Nephelo-Turbidity Meter 132, Systronics, India). (II) Trace metal analysis for total iron and total chromium was done after nitric acid digestion using a spectro-photometer, Hach, India. (III) Determination of total solid (TS), total dissolved solid (TDS) and total suspended solid (TSS) was done by a gravimetric method. (IV) Chemical oxygen demand (COD) determination was done by using a chemical oxygen demand analyzer, Hach, India and Vis spectrophotometer, Hach, India. The results of these analyses are important for determining the applicability of Ag-g-PHEMA as a flocculant for the treatment of municipal wastewater.

3 Results and discussion

3.1 Synthesis of Ag-g-(PHEMA) by a microwave assisted method

Ag-g-P(HEMA) was synthesized by a microwave assisted method. Various grades of the graft copolymer were synthesized by varying the ceric ammonium nitrate (CAN) and HEMA (monomer) concentrations. In each case, the microwave irradiation of the reaction mixture was continued until the mixture set into a viscous gel-like mass. The synthesis details are tabulated in Table 1.

The highest percent grafting and intrinsic viscosity (which is proportional to molecular weight) represent the optimal grade. From Table 1, it is obvious that the grafting was optimized for Ag-g-P(HEMA)-2 with a HEMA concentration of 10 g and a CAN concentration of 0.3 g.

In the presence of microwave radiation, only polar bonds are activated, leading to their rupture or cleavage which results in the formation of free radical sites. Ce (NH₄)₂(NO₃)₆ has been widely used for the oxidation of alcohols because it is an electron deficient molecule. It takes electrons from the alcoholic oxygens in agar and form a new bond i.e., Ce-O [6,42-47]. This bond is more polar than the O–H bond, so it breaks easily in the presence of microwave irradiation to form free radical sites on the backbone of the agar [36,38]. The generation of these free radicals initiates the 2-hydroxy ethyl methacrylate (HEMA) to form poly(2-hydroxyethylmethacrylate) (P (HEMA)) through propagation and termination. The P (HEMA) undergoes a grafting reaction resulting in the formation of PHEMA grafted agar. The proposed mechanism for the microwave assisted grafted Ag-g-P(HEMA) is depicted in Scheme 1.

3.2 Characterization

3.2.1 Intrinsic viscosities

The intrinsic viscosities were evaluated for the agar and the various grades of Ag-g-P(HEMA) and are shown in Table 1. Intrinsic viscosity is actually the hydrodynamic volume of the macromolecule in the solvent [29–39] (water in this case). Obviously the intrinsic viscosities of all the grades of Ag-g-P (HEMA) are greater than that of agar. This can be explained by the increase in the hydrodynamic volume due to the grafting of the P (HEMA) chains on the main polymer backbone (agar). Further, these results are in good agreement with Mark-Houwink-Sakurada relationship, intrinsic viscosity $\eta =$ KM^{α} , where K and α are constants, both related to the stiffness of the polymer chains [40]. This equation shows that the increase in intrinsic viscosity is the result of the increase in the molecular weight (M) due to the grafted HEMA chains. A graph showing the correlation between the percent grafting of Ag-g-P (HEMA) and the intrinsic viscosity is shown in Fig. 2. The intrinsic viscosity grows exponentially with % grafting. This function fits a curve with the equation $y = y_0 + Ax/t$.

Table 1 Synthesis details of different grades of poly(2-hydroxyethylmethacrylate) grafted agar (Ag-g-P(HEMA)

Graft copolymer grades	Wt of agar/g	Wt of HEMA/g	Wt of CAN/g	Time of microwave irradiation (up to gel formation)/s	Grafting/%	Intrinsic viscosity $/(dL \cdot g^{-1})$
Ag-g-P(HEMA)	1	10	0.2	0	0.00	0.00
Ag-g-P(HEMA)-1	1	10	0.2	82.3	200	4.44
Ag-g-P(HEMA)-2	1	10	0.3	78.77	835	10.66
Ag-g-(PHEMA)-3	1	10	0.4	60.2	476.4	5.35
Ag-g-P(HEMA)-4	1	5	0.3	93.3	648.56	7.96
Ag-g-P(HEMA)-5	1	15	0.3	81.21	329	5.24
Agar (Ag)	_	_	_	_	-	2.96

Grafted Poly (HEMA) chains on agar backbone

Scheme 1 Schematic representation of the mechanism for the "microwave assisted" synthesis of Ag-g-P(HEMA)

3.2.2 Elemental analysis

The results of elemental analysis for the agar and of the best grade of HEMA grafted agar (i.e., Ag-g-P(HEMA)-2) are given in Table 2. As expected, the Ag-g-P(HEMA)-2 elemental composition values are between those of agar and HEMA (its constituents).

3.2.3 FTIR spectroscopy

The FTIR spectrum of agar (Spectrum 3(a)) has a small

peak at 3170.97 cm⁻¹ which is due to the stretching vibrations of the primary alcohol (-CH₂OH) and a broad peak at 3572.17 cm⁻¹ which is due to the stretching vibrations of the secondary alcohol. The smaller peaks at 2980.02 and 2887.44 cm⁻¹ are due to C-H stretching vibrations. The band at 1068.56 cm⁻¹ can be attributed to C-O-C stretching vibrations. In the spectrum of Ag-g-P (HEMA)-2 (Spectrum 3 (b)), there is an additional peak at 1724.35 cm⁻¹ which is due to the C=O stretching vibrations from the grafted HEMA chains. This peak confirms the grafting of HEMA onto the agar. The FTIR

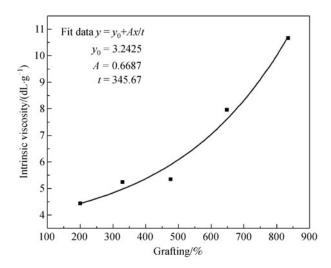


Fig. 2 Correlation between percent grafting of Ag-g-P (HEMA) and intrinsic viscosity. Fit data $y = y_0 + Ax/t$, where $y_0 = y$ offset, A = amplitude, t = time constant

Table 2 Elemental analysis

Polymer	C/%	H/%	O/%	N/%
Agar	46.93	5.7	46.93	0.00
HEMA	55.37	7.74	36.88	0.00
Ag-g-P(HEMA)-2	49.69	7.876	41.71	0.00

peaks of agar and Ag-g-PHEMA are summarized in Table 3.

3.2.4 Scanning electron microscopy analysis

The SEM micrographs of agar Fig. 4(a) and Ag-g-P (HEMA)-2 (the best grade) Fig. 4(b) show that a profound morphological change occurred in the Ag-g-P(HEMA)-2. The structures changed from a flaky structure in agar to a fibrillar structure in Ag-g-P(HEMA)-2 which took place because of the grafting of the HEMA chains onto the agar.

3.2.5 Flocculation study

3.2.5.1 Flocculation study in a kaolin suspension

The results of the flocculation study in a 0.25% kaolin suspension using the jar test apparatus are shown in Fig. 5. All the grades of grafted agar showed better flocculation efficacy than agar. This is as expected, due to their higher hydrodynamic volumes, i.e., intrinsic viscosities, (Table 1). A higher hydrodynamic volume of the macromolecule leads to a higher flocculation efficacy.

Among the various grades of Ag-g-P(HEMA), the optimized grade (Ag-g-P(HEMA)-2) showed the highest

flocculation efficacy due to its having highest hydrodynamic volume. A strong correlation between the percent grafting, the intrinsic viscosity and the flocculation efficacy is evident from Table 1 and Fig. 5. The correlation between these three fundamental factors is summarized in Table 4.

For all the polymers, there is an optimal dosage at which the flocculation efficacy is maximized. Above this dosage, destabilization of the flocs occurs due to over dosage of the flocculant. This trend in the flocculation curve confirms that a bridging mechanism [48] is behind this phenomenon.

According to the bridging mechanism, when long chain polymers are added to a colloidal suspension, they adsorb on two or more particle surfaces and form a bridge between them. There needs to be sufficient unoccupied space on the particle surface to form the polymer bridge. This phenomenon is observed up to a particular dosage of the polymer and at higher dosages the flocculation diminishes. This process is known as steric stabilization. At low polymer dosages, no significant bridging occurs and the flocculation efficacy remains low. At some minimum dosage, stabilization occurs and this is set as the optimum dosage for the polymer. Similarly at higher dosages of polymer or over dosage, there is insufficient surface area for the attachment of the polymer segments which leads to destabilization of the flocs. The optimal dosage of Ag-g-P (HEMA)-2 as a flocculant, in 0.25% kaolin suspension is 0.75 ppm.

3.2.5.2 Flocculation study in wastewater

The flocculation efficacy of the best grade of grafted agar (Ag-g-P(HEMA)-2) was optimized and compared to that of agar in municipal waste water using the standard jar test procedure. The flocculation efficacy was measured in terms of the reduction in the turbidity and the results are shown in Fig. 6.

Ag-g-P(HEMA)-2 showed a much higher flocculation efficacy than agar. The optimized dosage of flocculation for Ag-g-P(HEMA)-2 in the wastewater was found to be 0.75 ppm. Compared to agar, Ag-g-P(HEMA)-2 was found to considerably reduce the pollutant load in the wastewater as confirmed by the analysis of the supernatants drawn from the jar test procedure.

A comparative study of the water quality of the supernatants was done and the results are shown in Table 5. For the three samples, wastewater alone (SET 1), wastewater with 0.75 ppm of agar as the flocculant (SET 2) and wastewater with 0.75 ppm of Ag-g-P(HEMA)-2 as the flocculant (SET 3), the best water quality was achieved for SET 3. In SET 3, an appreciable reduction in the metal content (chromium VI & total iron) due to chelating with the hetero atoms in the main chain and the grafted P (HEMA) chains was observed. In addition there was a large reduction in the organic load (in terms of COD).

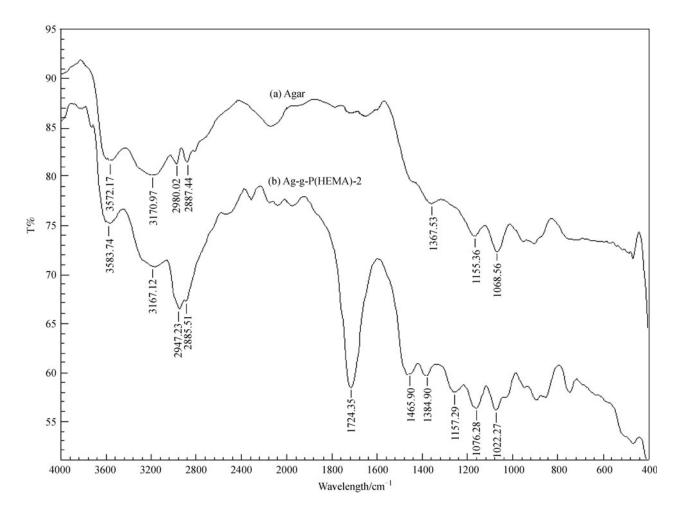


Fig. 3 FTIR spectra of (a) Agar and (b) Ag-g-P(HEMA)-2

Table 3 Significant FTIR stretching peaks/cm⁻¹

Polymer	$v_{\mathrm{O-H}}$	$v'_{\mathrm{O-H}}$	$v_{\mathrm{C-H}}$	$v_{\mathrm{C-O-C}}$	$v_{\rm C} = 0$
Agar (Ag)	3170.97	3572.17	2980.02, 2887.44	1068.56	-
Ag-g-P(HEMA)-2	3167.12	3583.74	2947.23, 2885.51	1078.28, 1022.27	1724.35

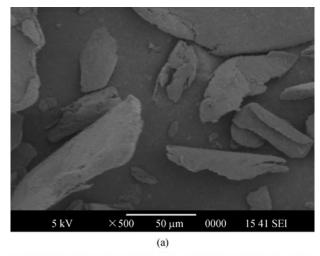
Thus, Ag-g-P(HEMA) is a much better flocculant than the starting material (agar). In addition, the reduction of TDS and TSS were much higher in the SET 3 sample. These results are in good agreement with the theory of flocculation.

4 Conclusions

A microwave-based grafting approach to modify natural polysaccharides (agar) can be used as a powerful tool for the development of valuable derivatives with tailor-made properties. Poly(2-hydroxyethylmethacrylate) grafted agar (Ag-g-P(HEMA)) has been synthesised by a novel 'microwave assisted' method, in which a combination of a chemical free radical initiator and microwave irradiation

was used to synthesize the graft copolymer. The synthesized grades of the graft copolymer were characterized through various physicochemical techniques. In addition, the flocculation efficacy of the graft copolymer in 0.25% kaolin suspension was studied using a standard 'jar test' procedure and the results were compared to those for the starting material (agar). The Ag-g-P(HEMA) grade with the highest hydrodynamic volume (i.e., intrinsic viscosity) had the best flocculation efficacy, as predicted by "Singh's easy approachability model" and "Brostow, Pal and Singh model of flocculation". The flocculation efficacy of the optimal grade of Ag-g-P(HEMA) was also investigated in municipal wastewater. The Ag-g-P (HEMA) was found as superior flocculant for reduction of the pollutant load in the waste water.

Overall, it may be concluded that current advancements



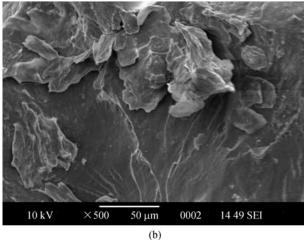


Fig. 4 SEM micrographs of (a) agar and (b) Ag-g-P(HEMA)-2

in the area of polysaccharide grafting using microwave irradiation have generated a method to obtain higher performance materials. Without having to compromise efficiency or yield, the microwave methodology helps achieve the goal of a clean technology which is simpler, cheaper, quicker and safer than the prevailing conventional methods.

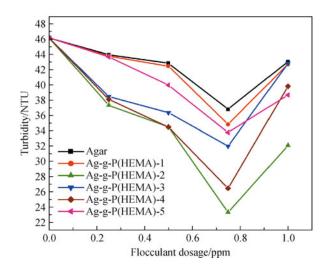


Fig. 5 Flocculation characteristics of Agar and the synthesized grades of Ag-g-P(HEMA) in a 0.25% kaolin suspension

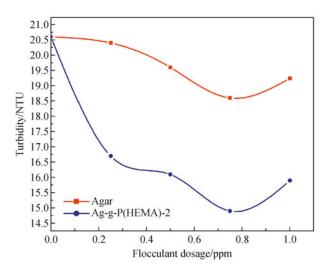


Fig. 6 Flocculation characteristics of the agar and of the best grade of Ag-g-P(HEMA) in wastewater

Table 4 Correlation between percent grafting, intrinsic viscosity and flocculation efficacy for the microwave assisted synthesized Ag-g-P(HEMA) grades

Polymer grade	Percentage grafting/(G%)	Intrinsic viscosity/(dL·g ⁻¹)	Flocculation efficacy (in terms of percent reduction of turbidity in a 0.25% kaolin suspension at optimized dosage 0.75 ppm)/%
Agar	=	2.96	20.28
Ag-g-P(HEMA)-1	200	4.44	24.56
Ag-g-P(HEMA)-5	329	5.24	26.83
Ag-g-P(HEMA)-3	476.4	5.35	30.73
Ag-g-P(HEMA)-4	648.54	7.96	42.70
Ag-g-P(HEMA)-2	835	10.66	49.52

Parameters	SET 1	SET 2	SET 3
Turbidity/NTU	20.6	18.62	14.9
TDS/ppm	336	280	220
TSS/ppm	134	78	50
Total iron/ppm	1.93	1.89	1.13
Total chromiumVI/ppm	0.141	0.023	0.005
COD/ppm	609.09	290.90	81.81

Table 5 Comparative study of the performance of the best grade of Ag-g-P(HEMA) for the treatment of municipal wastewater

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References

- 1. Wuttisela K, Panijpan B, Triampo W, Triampo D. Optimization of the water absorption by crosslinked agar-g-poly(acrylic acid). Polymer (Korea), 2008, 32(6): 537–543
- Labropoulos K C, Niesz D E, Danforth S C, Kevrekidis P G. Dynamic rheology of agar gels: Theory and experiments. Part I: Development of a rheological model. Carbohydrate Polymers, 2002, 50(4): 393–406
- Armisen R, Galatas F. Properties and uses of agar, production and utilization of products from commercial seaweeds (Ch. 1). Fisheries and Aquaculture Organization, 1987, 288: 1–57
- 4. Odian G. Principles of polymerization (3rd edition). New York: John wiley & sons, 1991, 2: 17–19
- Gowariker V R, Viswanathan N V, Sreedhar J. Polymer Science.
 New Delhi: New age International (p) Ltd, 1986, 91–92
- Bhattacharya A, Rawlins J W, Ray P. Polymer Grafting and Crosslinking. New Jersey: John Wiley & Sons, 2008, 1–329
- Da Silva D A, de Paula R C M, Feitosa J P A. Graft copolymerization of acrylamide onto cashew gum. European Polymer Journal, 2007, 43(6): 2620–2629
- Mostafa K A. Graft polymerization of acrylic acid onto starch using potassium permanganate acid (redox system). Journal of Applied Polymer Science, 1995, 56(2): 263–269
- Rani U G, Mishra S, Sen G, Jha U. Polyacrylamide grafted agar: Synthesis and applications of conventional and microwave assisted technique. Carbohydrate Polymers, 2012, 90(2): 784–791
- Bharti S, Mishra S, Sen G. Ceric ion initiated synthesis of polyacrylamide grafted oatmeal: its application as flocculant for waste water treatment. Carbohydrate Polymers, 2013, 93(2): 528– 536
- 11. Gupta K C, Sahoo S. Graft copolymerization of acrylonitrile and ethylmethacrylate comonomers on cellulose using ceric ions. Biomacromolecules, 2001, 2(1): 239–247
- 12. Sen G, Pal S. Polyacrylamide grafted carboxymethyltamarind (CMT-g-PAM): development and application of a novel polymeric flocculant. Macromolecular Symposia, 2009, 277(1): 100–111
- 13. Huang R Y M, Immergut B, Immergu E H, Rapson W H. Grafting vinyl polymers onto cellulose by high energy radiation. I. High

- energy radiation-induced graft copolymerization of styrene onto cellulose. Journal of Polymer Science: Part A, General Papers, 2003, 1(4): 1257–1270
- Hebeish A, Mehta P C. Grafting of acrylonitrile to different cellulosic materials by high-energy radiation. Textile Research Journal, 1968, 38(10): 1070–1071
- Geresh S, Gdalevsky G Y, Gilboa I, Voorspoels J, Remon J P, Kost J. Bioadhesive grafted cellulose copolymers as platforms for per oral drug delivery: a study of theophylline release. Journal of Controlled Release, 2004, 94(2-3): 391–399
- Shiraishi N, Williams J L, Stannett V. The radiation grafting of vinyl monomers to cotton fabrics. I. Methacrylic acid to terry cloth towelling. Radiation Physics and Chemistry, 1982, 19: 73–78
- Sharma R K, Misra B N. Grafting onto wool. Polymer Bulletin, 1981, 6(3-4): 183–188
- Carenza M. Recent achievements in the use of radiation polymerization and grafting for biomedical applications. Radiation Physics and Chemistry, 1992, 39: 485–493
- Wang J P, Chen Y Z, Zhang S J, Yu H Q. A chitosan-based flocculant prepared with gamma-irradiation-induced grafting. Bioresource Technology, 2008, 99(9): 3397–3402
- 20. Barsbay M, Guven O, Davis T P, Kowollik C B, Barner L. RAFT-mediated polymerization and grafting of sodium 4-styrenesulfonate from cellulose initiated via γ -radiation. Polymer, 2009, 50(4): 973–982
- Deng J, Wang L, Liu L, Yang W. Developments and new applications of UV-induced surface graft polymerizations. Progress in Polymer Science, 2009, 34(2): 156–193
- Wang J, Liang G, Zhao W, Lu S, Zhang Z. Studies on surface modification of UHMWPE fibers via UV initiated grafting. Applied Surface Science, 2006, 253(2): 668–673
- Hua H, Li N, Wu L, Zhong H, Wu G, Yuan Z, Lin X, Tang L. Antifouling ultrafiltration membrane prepared from polysulfone-graftmethyl acrylate copolymers by UV-induced grafting method. Journal of Environmental Sciences (China), 2008, 20(5): 565–570
- Shanmugharaj A M, Kim J K, Ryu S H. Modification of rubber surface by UV surface grafting. Applied Surface Science, 2006, 252 (16): 5714–5722
- Zhu Z, Kelley M J. Grafting onto poly(ethylene terephthalate) driven by 172 nm UV light. Applied Surface Science, 2005, 252(2): 303–310
- Deng J, Yang W. Grafting copolymerization of styrene and maleicanhydride binary monomer systems induced by UV irradiation. European Polymer Journal, 2005, 41(11): 2685–2692

- Thaker M D, Trivedi H C. Ultraviolet-radiation-induced graft copolymerization of methyl acrylate onto the sodium salt of partially carboxymethylated guar gum. Journal of Applied Polymer Science, 2005, 97(5): 1977–1986
- Chen C, Li X, Li Z. Graft copolymerization of acrylamide onto the UV-Ray irradiated film of polyester-polyether. Chinese Journal of Polymer Science, 1988, 6: 1
- Mishra S, Rani G U, Sen G. Microwave initiated synthesis and application of poly acrylic acid grafted carboxymethylcellulose. Carbohydrate Polymers, 2012, 87(3): 2255–2262
- Mishra S, Sen G. Microwave initiated synthesis of polymethylmethacrylate grafted guar (GG-g-PMMA), characterizations and application. International Journal of Biological Macromolecules, 2011, 48(4): 688–694
- Sen G, Mishra S, Jha U, Pal S. Microwave initiated synthesis of polyacrylamide grafted guar gum (GG-g-PAM)—characterizations and application as matrix for controlled release of 5-amino salicylic acid. International Journal of Biological Macromolecules, 2010, 47 (2): 164–170
- 32. Sen G, Kumar R, Ghosh S, Pal S. A novel polymeric flocculant based on polyacrylamide grafted carboxymethylstarch. Carbohydrate Polymers, 2009, 77(4): 822–831
- Sen G, Singh R P, Sagar P. Microwave-initiated synthesis of polyacrylamide grafted sodium alginate: synthesis and characterization. Journal of Applied Polymer Science, 2010, 115(1): 63–71
- Sen G, Mishra S, Rani G U, Rani P, Prasad R. Microwave initiated synthesis of polyacrylamide grafted Psyllium and its application as a flocculent. International Journal of Biological Macromolecules, 2012, 50(2): 369–375
- 35. Sen G, Pal S. Microwave initiated synthesis of polyacrylamide grafted carboxymethylstarch (CMS-g-PAM): Application as a novel matrix for sustained drug release. International Journal of Biological Macromolecules, 2009, 45(1): 48–55
- 36. Mishra S, Sen G, Rani G U, Sinha S. Microwave assisted synthesis

- of polyacrylamide grafted agar (Ag-g-PAM) and its application as flocculant for wastewater treatment. International Journal of Biological Macromolecules, 2011, 49(4): 591–598
- Mishra S, Mukul A, Sen G, Jha U. Microwave assisted synthesis of polyacrylamide grafted starch (St-g-PAM) and its applicability as flocculant for water treatment. International Journal of Biological Macromolecules, 2011, 48(1): 106–111
- Rani P, Sen G, Mishra S, Jha U. Microwave assisted synthesis of polyacrylamide grafted gum ghatti and its application as flocculant. Carbohydrate Polymers, 2012, 89(1): 275–281
- 39. Rani P, Mishra S, Sen G. Microwave based synthesis of polymethyl methacrylate grafted alginate: its application as flocculant. Carbohydrate Polymers, 2013, 91(2): 686–692
- Sen G, Sharon A, Pal S. Grafted polysaccharides: smart materials of the future, their synthesis and applications (Chapter 05). USA: Wiley-Scrivener, 2011, 99–128
- Tripathy T, Ranjan De B. Flocculation: a new way to treat the waste water. Journal of Physiological Sciences; JPS, 2006, 10: 93–127
- Mc Dowall D J, Gupta B S, Stannnett V T. Grafting of vinyl monomers to cellulose by ceric ion initiation. Progress in Polymer Science, 1984, 10(1): 1–50
- Singh J, Yadav L D S. Organic Synthesis. A pragati Prakadshan, 2008, 1–652
- 44. Odian G. Principles of Polymerization (4th edition). New York: John Wiley & Sons, 2004, 1–832
- Nayak P L, Lenka S. Redox polymerization initiated by metal ions.
 Journal of macromolecule Science, Part C: Polymer review, 1980, 19(1): 83–134
- Misra G S, Bajpai U D. Redox polymerization. Progress in Polymer Science, 1982, 8(1-2): 61–131
- Temel O, Ismail C. Synthesis of block copolymers via redox polymerization process: a critical review. Iranian Polymer Journal, 2007, 16(8): 561–581
- 48. Ruehrwein R A, Ward D W. Mechanism of clay aggregation by poly electrolytes. Journal of Soil Science, 1952, 73(6): 485–492