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Ceric ion-induced synthesis of polymethyl methacrylate-grafted oatmeal: its characterizations and applications

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ABSTRACT

The present studies report the synthesis of a novel graft copolymer "polymethyl methacrylate-grafted oatmeal" (OAT-g-PMMA) using "conventional" technique. Grafting of PMMA chains on the backbone of parent biopolymer (oatmeal) was confirmed through various physicochemical techniques like intrinsic viscosity, FTIR, elemental analysis (C, H, N, S and O), scanning electron microscopy, thermal gravimetric analysis, number-average molecular weight, solubility, ^{13}C-CP/MAS solid-state NMR spectroscopy and P-XRD. The intrinsic viscosity of oatmeal substantially improved after grafting of PMMA chains. The grafted biopolymers were assessed for its implication as a potential flocculant by standard "jar test" and "settling test" protocol. Flocculation characteristics of the synthesized OAT-g-PMMA were compared with parent biopolymer (oatmeal) and alum in 0.25 wt.% kaolin suspension and then in municipal wastewater through standard "jar test" protocol which showed encouraging results.

Keywords: Biopolymers; "Conventional" synthesis; Graft copolymers; ^{13}C-CP/MAS solid-state NMR spectroscopy; Flocculant; "Jar test" protocol; Municipal wastewater treatment

1. Introduction

Water is possibly the most essential resource on this planet. Availability of fresh water has a key role in establishment of all significant civilizations. Its access is deciding factor for all industries whether it is a traditional cottage industry or a multinational company. The demand for clean water resources is surpassing all limits. In this bleak scenario of water dearth, recycling of wastewater gains more and more significance for non-potable applications [1]. Recycled wastewater can be used for numerous purposes including landscape irrigation, fire protection, toilet flushing, agricultural irrigation, cooling and air conditioning [2–4]. Particulate matters are one of the most

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significant pollutants in wastewater and pose an obstacle during their treatment [5–10]. So, primary requirement towards any wastewater treatment is the removal of suspended particulates. It has been observed that removal of particulates drastically reduces the overall concentration of various contaminants like metallic contaminants, organic load and colour. An ever growing demand of eco-friendly separation technologies promotes the interest in usage of biodegradable, non-toxic flocculants derived from natural renewable raw materials [11]. The polymers used in flocculation courses are commonly synthetic polymethyl methacrylate, polyacrylamide, polyacrylic acid and their derivatives [12–16]. Flocculation is broadly used in various fields of industry, including wastewater treatment or sludge dewatering [17,18] and can be easily incorporated in any standard wastewater treatment plant, without the need for any significant infrastructure [19–25]. It is a course in which destabilized particles are induced to come together to form larger agglomerates by adding minute quantity of chemicals called flocculants [19,26]. Earlier chemical coagulants (alum) were being used, which were less effective and required larger dosage [20]. Since the introduction of synthetic polymeric flocculants, they are being used to treat municipal wastewater. They are highly efficient due to their superior molecular weight (MW), more branches and better potential to adsorb onto suspended particles in wastewater [26]. Properties of natural and synthetic biopolymers can be modified through grafting. Recently, a new class of flocculating agents based on graft copolymers has been reported [22,27–42]. Polyacrylamide-grafted oatmeal as a flocculant has also been reported [28]. The term "conventional" technique [28,43] refers to a process of graft copolymer synthesis which is based on free radical mechanism using chemical free radical initiator to generate free radical sites on the backbone of biopolymer [44–48]. Among various polymerization techniques used in synthesis of graft copolymers, the most recent and popular one involves the ceric ion-initiated radical copolymerization [4,43,49–51]. Ceric (IV) salts are found to be very effective redox systems, capable of producing free radicals, thus initiating graft polymerization and minimizing homopolymer formation [5,52–56].

Oatmeal is gelatinous biopolymer made from β-D-glucan, a soluble fibre of monosaccharide "D-glucose". The bonds between the D-glucose or D-glucopyranosyl are either be β-1, 3 or β-1, 4 linkages. The (1 → 3)-linkage breaks up the homogeneous construction of β-D-glucan and makes it soluble and stretchy [57]. Avenalin is the key storage protein in oatmeal. The most important properties of oatmeal are viscosity enhancement and flocculation. It has high shear potency. No article has been reported on synthesis of polymethyl methacrylate-grafted oatmeal as a graft copolymer via "conventional" technique to the best of our knowledge. The present investigation is carried out by modification of oatmeal towards its exploration as potential flocculant to treat municipal wastewater. It involves fusion of polymethyl methacrylate on backbone of oatmeal biopolymer via "conventional" technique using ceric ammonium nitrate (CAN). At low temperature, CAN is more competent because of its instability at higher temperature [58]. The objectives were to reduce the concentration of heavy metals, organic loads, suspended particulates and colour present in municipal wastewater. The results of novel flocculant are beneficial to improve environmentally safe water quality through flocculation system.

2. Materials and methods

2.1. Materials

Oatmeal: Shanti Food Chem. Pvt. Ltd., Rajkot, Gujarat, India. Methyl methacrylate: CDH, New Delhi, India. CAN: E. Merck (India), Mumbai, India. Acetone: Rankem, New Delhi, India. All the chemicals were used as received; without further purification.

The wastewater was collected from the main sewage system of BIT-Mesra society.

2.2. Synthesis of graft copolymer

2.2.1. "Conventional" synthesis of polymethyl methacrylate-grafted oatmeal (OAT-g-PMMA)

Grafting reaction was carried out by ceric ion-induced redox initiation method [59]. One gram of oatmeal was dissolved in 40 mL distilled water with constant stirring and purging with nitrogen. Desired amount of methyl methacrylate was added to the oatmeal suspension. They were mixed well and were transferred to the reaction vessel (250 mL borosil beaker). The oxygen-free nitrogen gas was purged through the solution mixture followed by addition of catalytic amount of CAN of preferred concentration and as nitrogen purging was continued. The reaction was continued for 24 h. The reaction temperature was maintained at room temperature.

Subsequently, the gel-like mass left in the reaction vessel was poured into excess of acetone. This was done to minimize the probability of competing homopolymer formation reaction. The precipitated graft copolymers were recovered and air dried for moisture removal and collected. The synthesis details of various grades of the graft copolymer have been shown in Table 1. The percentage grafting and percentage grafting efficiency were evaluated as:

$$\% \, G = \frac{\text{Wt. of graft copolymer} - \text{Wt. of biopolymer}}{\text{Wt. of biopolymer}} \times 100 \tag{1}$$

$$\% \, \text{GE} = \frac{\text{Wt. of graft copolymer} - \text{Wt. of biopolymer}}{\text{Wt. of monomer}} \times 100 \tag{2}$$

Any occluded polymethyl methacrylate (PMMA) formed due to competing homopolymer formation reaction was removed by extraction with acetone for 24 h [60]. The mechanism of synthesis of the graft copolymer has been given in Fig. 1.

2.3. Characterization

2.3.1. Intrinsic viscosity measurement

Intrinsic viscosity measurements of the polymer solutions were carried out with an Ubbelohde viscometer (capillary diameter 0.46 mm) at 25°C. The viscosities were measured in neutral aqueous solutions. The time of flow for solutions was measured at four different concentrations (0.1, 0.05, 0.025 and 0.0125%). From the time of flow of polymer solutions (t) and that of the solvent (t_0, for distilled water), relative viscosity ($\eta_{\text{rel}} = t/t_0$) was obtained. Specific viscosity (η_{sp}), relative viscosity (η_{rel}), reduced viscosity (η_{red}) and inherent viscosity (η_{inh}) were mathematically calculated as:

$$\eta_{\text{rel}} = t/t_0 \tag{3}$$

$$\eta_{\text{sp}} = \eta_{\text{rel}} - 1 \tag{4}$$

$$\eta_{\text{red}} = \eta_{\text{sp}}/C \tag{5}$$

$$\eta_{\text{inh}} = \ln \eta_{\text{rel}}/C \tag{6}$$

where C represents polymer concentration in g/dL.

Subsequently, the reduced viscosity (η_{red}) and the inherent viscosity (η_{inh}) were simultaneously plotted against concentration [61]. The intrinsic viscosity was obtained from the point of intersection after extrapolation of two plots (i.e.η_{red} vs. C and ln η_{inh} vs. C) to zero concentration. The intrinsic viscosity thus evaluated for various grades of the graft copolymer is reported in Table 1.

Table 1
Synthesis detail of OAT-g-PMMA

Polymer grade	Wt. of oatmeal (g)	Wt. of methyl methacrylate (g)	Wt. of CAN (g)	% Grafting (%G)	% Grafting efficiency (%GE)	Intrinsic viscosity (dL/g)	Number-average molecular weight (kDa)	% Flocculation efficacy	Solubility (g/L)	
									In H_2O	In n-hexane
OAT-g-PMMA-1	1	10	0.1	25	2.5	1.4	357	29.19	3.29	2.33
OAT-g-PMMA-2	1	10	0.2	50	5	2.22	511	39.88	3.61	2.84
OAT-g-PMMA-3	1	10	0.3	35	3.5	2.05	381	34.78	3.37	2.77
OAT-g-PMMA-4	1	5	0.2	20	4	1.06	288	23.14	3.05	2.29
OAT-g-PMMA-5	1	15	0.2	123	8.2	4.62	680	70.29	5.49	4.78
OAT-g-PMMA-6	1	20	0.2	110	5.5	3.16	651	54.73	5.23	4.55
Oatmeal (OAT)	–	–	–	–	–	0.87	212	19.09	2.9	2.02
Alum	–	–	–	–	–	–	–	11.59	–	–

2.3.2. Elemental analysis

The elemental analysis of oatmeal and that of OAT-g-PMMA-5 (best grade of the grafted oatmeal synthesized) was done by an Elemental Analyzer (Make-M/s Elementar, Germany; Model-Vario EL III). The estimation of five elements, i.e. carbon, hydrogen, nitrogen, oxygen and sulphur were undertaken. The results have been summarized in Table 2.

2.3.3. FTIR spectroscopy

The combined FTIR and OAT-g-PMMA-5 (Fig. 2) were recorded by solid state, by KBr pellet method using a FTIR spectrophotometer (Model IR-Prestige 21, Shimadzu Corporation, Japan) between 400 and 4,000 cm^{-1} at a resolution of 4 cm^{-1}.

2.3.4. Scanning electron microscopy

Surface morphology of oatmeal (Fig. 3(a)) and OAT-g-PMMA-5 (Fig. 3(b)) were analysed in Scanning electron microscopy (SEM) in powdered form (Model: JSM-6390LV, Jeol, Japan).

2.3.5. Thermal gravimetric analysis (TGA) Studies

The combined Thermal gravimetric analysis (TGA) curve of oatmeal and OAT-g-PMMA-5 (Fig. 4) was carried out with TGA instrument (Model: DTG-60; Shimzadu, Japan). The study was performed in an inert atmosphere (nitrogen) from 25 to 800˚C. The heating rate was uniform in all cases at 5˚/min.

2.3.6. Determination of number-average MW

The number-average MW of oatmeal and various grades of OAT-g-PMMA were determined in aqueous medium by osmometer (A + Adv. Instruments, INC. Model 3320, Osmometer). The correlation between the three parameters i.e. percentage grafting (%*G*), intrinsic viscosity and number-average MW is depicted in (Fig. 5).

Table 2
Elemental analysis

Polymer grade	%C	%H	%N	%O	%S
PMMA	60.59	7.12	0.00	32.29	0.00
Oatmeal	43.58	8.47	2.192	45.47	0.297
OAT-g-PMMA-5	47.32	7.99	1.66	42.808	0.222

2.3.7. Solubility studies

The solubility of oatmeal and the synthesized grades of OAT-g-PMMA were determined in polar and non-polar medium by standard gravimetric procedure at 25˚C. The aqueous medium used was of neutral pH. The solubility study for oatmeal and various grades of OAT-g-PMMA has been correlated with their respective percentage grafting. The solubility details of oatmeal and diverse grades of OAT-g-PMMA in polar and non-polar solvent have been graphically compared and represented in Fig. 6.

2.3.8. Zeta potential determination

Zeta potential of 0.25 wt.% kaolin Suspension using blank (without flocculant) and optimized best grade and dosage of OAT-g-PMMA (i.e. grade 5) at pH 7, 10 and 4 were determined in aqueous solution via light scattering measurement (Make and Model: Malvern Inst., UK; Nano ZS) at measurement angle is 173˚ and temperature 2–90˚C and the comparative graph of zeta potential at variable pH in 0.25% kaolin is represented in Fig. 7 and data are tabulated in Table 3.

2.3.9. ^{13}C-CP/MAS solid-state NMR spectroscopy

The ^{13}C-CP/MAS solid-state NMR spectra of oatmeal (Fig. 8(a)) and OAT-g-PMMA-5 (Fig. 8(b)) was recorded in solid state at 400 MHz Spectrometer Frequency, 298 K (i.e. 25˚C) Temperature, (Make and Model: JEOL ECX-II-400 MHz spectrometer) from −10 to 240 ppm spectral width. The ^{13}C-CP/MAS NMR spectrum of OAT-g-PMMA-5 was assigned by taking oatmeal as reference.

2.3.10. Powder X-ray diffraction measurements

Powder X-ray diffraction studies of oatmeal (Fig. 9(a)) and OAT-g-PMMA-5 (Fig. 9(b)) were

Table 3
Zeta potential data in 0.25 wt.% kaolin suspension w.r.to pH 7, 10 and 4 using blank and OAT-g-PMMA-5

S. no.	Polymer grade	pH	Suspension applied	Zeta potential (mV)
1	Blank (without flocculant)	7	0.25 wt.% kaolin suspension	−24.7
2	OAT-g-PMMA-5 (1.28 ppm)	7	0.25 wt.% kaolin suspension	−20.9
3	OAT-g-PMMA-5 (1.28 ppm)	10	0.25 wt.% kaolin suspension	−22.1
4	OAT-g-PMMA-5 (1.28 ppm)	4	0.25 wt.% kaolin suspension	−17.9

performed under ambient conditions, by a X-ray diffractometer (Make and Model: Rigaku smartlab, 9 kW) using Cu Kα1 (λ = 1.54056 Å) radiation (scan type: locked coupled: scan mode: continuous; step size: 0.02°). The tube voltage and amperage were set at 35 kV and 70 mA, respectively. Each sample was scanned between 5° and 50° at 2θ scale.

2.4. Application of the grafted biopolymer as potential flocculant for treating municipal wastewater

2.4.1. Flocculation characteristics in kaolin suspension

OAT-g-PMMA were used as a flocculant for 0.25 wt.% kaolin suspension and municipal wastewater (collected from BIT-Mesra, Municipality). Flocculation investigations were carried out by standard "jar test" protocol using "jar test" apparatus (Make: Simeco, Kolkata, India). The test protocol involved taking a measured quantity (800 mL) in one litre borosil® beakers. Calculated amount of the flocculant (oatmeal or various grades of OAT-g-PMMA) or alum was added in concentrated solution form to achieve the desired dosage (ranging from 0 to 1.60 ppm). The solutions were identically stirred in "jar test" apparatus at 150 rpm for 30 s, 60 rpm for 5 min, followed by 15 min of settling time [62]. Afterwards, supernatant liquid was collected and turbidity was measured in nephelo-turbidity meter (Digital Nephelo-Turbidity Meter 132, Systronics, India). The flocculation efficacy studied for oatmeal, alum and various grades of OAT-g-PMMA has been graphically compared in Fig. 10a. The optimized dosage in each case is indicated by the minima of the curve. Flocculation curves of OAT-g-PMMA-5 (Best Grade) w.r.to oatmeal and alum has been graphically presented in Fig. 10b.

Settling test employs a 100 mL stoppered graduated cylinder containing 0.25 wt.% kaolin suspensions. The flocculant (OAT-g-PMMA or oatmeal) was added in form of concentrated solution to affect the optimized dose (as determined by the "jar test" protocol above). The cylinder was mixed thoroughly by turning it upside down 10 times. Then, the cylinder was set upright, kept undisturbed and height of the clear water suspension interface monitored w.r.to time. The result is graphically plotted as interfacial height vs. settling time (Fig. 10c) and thus the settling rate were computed.

2.4.2. Flocculation studies in municipal wastewater

The flocculation efficacy of OAT-g-PMMA-5 and that of oatmeal were studied in municipal wastewater by standard "jar test" protocol. The experiment was done in three sets.

SET 1: municipal wastewater without flocculant.
SET 2: municipal wastewater with 1.28 ppm of oatmeal.
SET 3: municipal wastewater with 1.28 ppm of OAT-g-PMMA-5.

The water quality of these supernatants was analysed by standard procedures [63], as reported in Table 4. Removal of colour from municipal wastewater was also studied using colorimeter (Fig. 10d).

2.4.3. Chemical analysis of the supernatant liquids

The supernatant liquids drawn from the three sets of experiments were subjected to the following chemical/environmental analysis:

Table 4
Result of municipal wastewater treatment

Parameter	Supernatant liquid SET 1 [wastewater without flocculant]	Supernatant liquid SET 2 [wastewater with 1.28 ppm of oatmeal]	Supernatant liquid SET 3 [wastewater with 1.28 ppm of OAT-g-PMMA-5]
Turbidity (NTU)	65.02	45.49	32.01
TS (ppm)	771	588	435
TDS (ppm)	632	420	380
TSS (ppm)	139	105	88
BOD_5 (ppm)	202	177	100
COD (ppm)	477	371	288
Cr (ppm)	4.08	3.87	2.02
Fe (ppm)	8.24	8.04	3.67
Mn (ppm)	0.355	0.349	0.144
Ni (ppm)	0.456	0.443	0.310

(1) Turbidity testing using calibrated nephelo-turbudity meter (Digital Nephelo-Turbidity Meter 132, Systronics, India).
(2) Trace metal analysis for Fe, Mn, Ni and Cr; after nitric acid digestion by spectrophotometric method [63], using (ELICO® double beam SL 210 UV–vis Spectrophotometer).
(3) Determination of total Solid (TS), total dissolved solid (TDS) and total suspended solid (TSS); by gravimetric method [63].
(4) COD determination by chemical oxygen demand analyzer, Hach, India and (ELICO® double beam SL 210 UV–vis Spectrophotometer).
(5) BOD_5 was also estimated by quantitative analysis using standard procedure [63].
(6) Colour measurements using colorimeter.

The results of these analyses are important for determination of applicability of OAT-g-PMMA-5 as a novel flocculant for treatment of municipal wastewater which have been summarized in Table 4.

3. Results and discussion

3.1. Synthesis of OAT-g-PMMA using "conventional" technique

OAT-g-PMMA has been synthesized using "conventional" technique. Various grades of the graft copolymer were synthesized by varying CAN and monomer concentration. The synthesis details have been tabulated in Table 1. The optimized grade has been determined through its higher percentage grafting and intrinsic viscosity (which is proportional

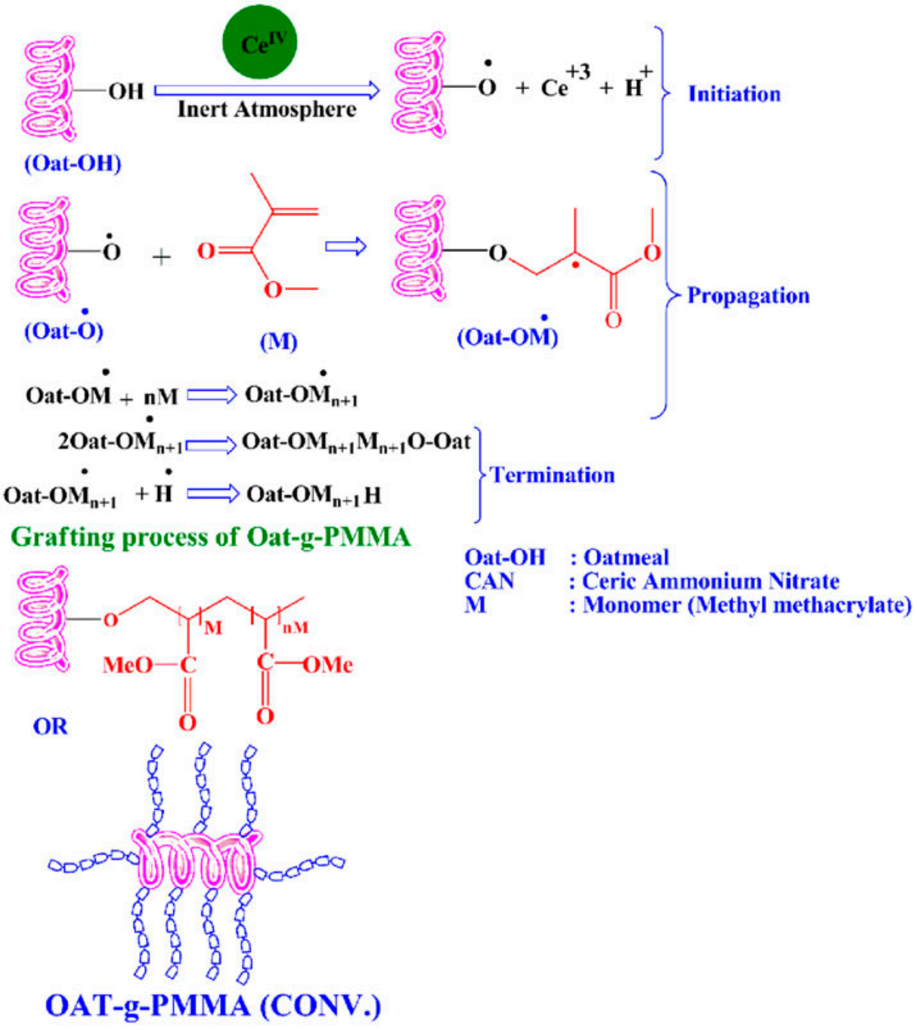

Fig. 1. Schematic representation of mechanism for "conventional" synthesis of OAT-g-PMMA.

to MW according to Mark–Houwink–Sakurada relationship). The synthesis approach involved optimization w.r.to CAN, keeping the methyl methacrylate concentration constant (i.e. OAT-g-PMMA-1, OAT-g-PMMA-2 and OAT-g-PMMA-3); followed by optimization w.r.to methyl methacrylate, keeping the CAN concentration as optimized before (i.e. OAT-g-PMMA-2, OAT-g-PMMA-4, OAT-g-PMMA-5 and OAT-g-PMMA-6). From Table 1, it is obvious that the grafting is optimized at methyl methacrylate concentration of 15 g and CAN concentration of 0.2 g in the reaction mixture (~40 mL).

In the crystal structure of CAN, Cerium (IV) is surrounded by oxygen atoms from six-bidentate nitrate ions resulting in a 12-coordinate icosahedral geometry [64]. Cerium (IV) takes electrons from C-6 alcoholic oxygen in oatmeal to form a new Ce–O bond that is predominantly ionic in character owing to its large size. This new bond being more polar than –O–H bond, cleaves readily to form free radical site on the backbone of oatmeal from where the graft chains grow by the addition of acrylic monomer (i.e. methyl methacrylate). Mechanism of “conventional” synthesis of graft copolymers has been reported in former studies [28,43,53,58]. The planned mechanism for the synthesis of graft copolymers using “conventional” technique has been depicted in Fig. 1.

3.1.1. Effect of initiator (CAN) concentration over percentage grafting (%G)

A low concentration of initiator a few grafting sites which may result in longer PMMA chain, on the high contrary, it will initiate a larger number of grafting sites [43]. The effect of initiator concentration on percentage grafting (%G) has been graphically compared and represented in Fig. 11.

3.1.2. Effect of monomer (MMA) concentration over percentage grafting (%G)

Percentage grafting increases with increase in monomer concentration up to certain extent and then decreases. This behaviour may be due to more monomer molecules grafted on the backbone of biopolymer [43]. The effect of monomer (MMA) concentration on percentage grafting (%*G*) has been graphically compared and reported in Fig. 12.

3.2. Characterization

3.2.1. Intrinsic viscosity

As evident from Table 1, intrinsic viscosities of all the grades of OAT-g-PMMA are greater than oatmeal confirming the grafting process. This is due to the increase in hydrodynamic volume resulting from grafting of the PMMA chains on the oatmeal. These PMMA chains increase hydrodynamic volume either by their own contribution or by uncoiling of the biopolymer chains through steric hindrance to intra molecular bonding. This is in agreement with Mark–Houwink–Sakurada relationship (intrinsic viscosity $\eta = KM^{\alpha}$, where K and α are constants, both related to inflexibility of the polymer chains). Hence, increase in intrinsic viscosity is due to increase in MW as a result of grafting.

3.2.2. Elemental analysis

The results of elemental analysis for oatmeal (OAT), PMMA and that of the best grade of PMMA-grafted oatmeal (OAT-g-PMMA-5) are given in Table 2. The data clearly shows that the grafted product has an elemental composition which is intermediate of its constituents (OAT and PMMA).

3.2.3. FTIR spectroscopy

Oatmeal has two O–H stretching peaks at 3,759.26 and 3,560.59 cm^{-1}, which may be due to the stretching vibration of 1° and 2° –O–H (Fig. 2). One peak at 3,275.13 cm^{-1} can be attributed to N–H stretching vibration due to the presence of protein content in oatmeal. Peaks at 2,927.92 and 2,856.58 cm^{-1} are assigned to the C–H stretching vibrations. The peak at 1,745.58 cm^{-1} is due to C=O stretching vibrations, N–H bending peak at 1,662.64 cm^{-1} and C–N bending peaks at 1,338.60 cm^{-1}.

From Fig. 2, it is also clear that all the above peaks present in oatmeal are also present in OAT-g-PMMA-5 apart from the peaks due to 1 and 2° –O–H stretching vibrations. The peaks 3,759.26 and 3,560.59 cm^{-1} are present in case of oatmeal are not present in OAT-g-PMMA-5; thus confirming the grafting process.

3.2.4. SEM analysis

It is evident that profound morphological change from granular structure of oatmeal (Fig. 3(a)) to fibrillar structure of OAT-g-PMMA-5 (Fig. 3(b)) has taken place. This can be well explained in terms of grafting phenomenon i.e. after addition of PMMA chains on the main backbone of parent biopolymer (oatmeal) the granular morphology has been transformed. The changes in the surface morphology confirm the grafting of PMMA onto oatmeal backbone.

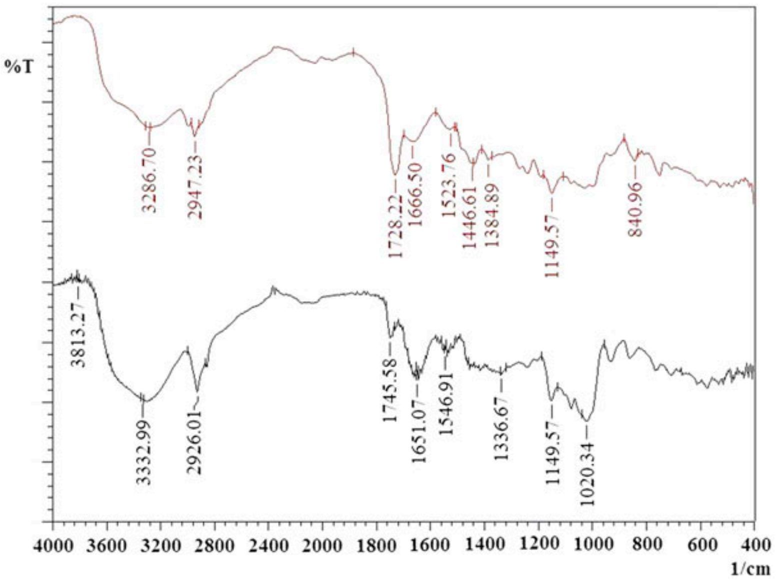

Fig. 2. Combined FTIR spectrum of oatmeal and OAT-g-PMMA-5.

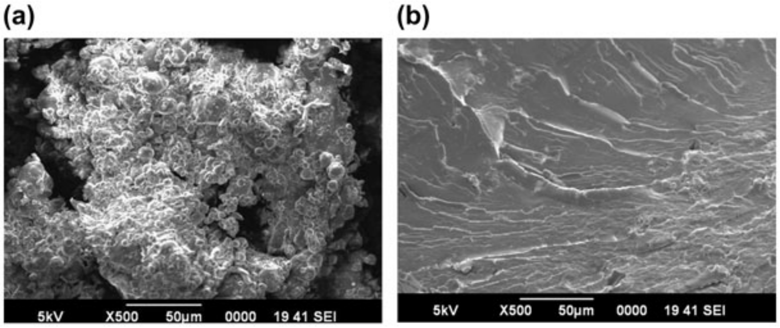

Fig. 3. SEM morphology of (a) oatmeal (500 × magnification) and (b) OAT-g-PMMA-5 (500 × magnification).

3.2.5. Thermal gravimetric analysis

In case of oatmeal, three distinct zones of weight loss are observed. The initial weight loss (25–225˚C) is due to the presence of small amount of moisture in the sample. The second zone (225–465˚C) is a result of decomposition of biopolymer and the third zone (465–800˚C) weight loss corresponds to complete degradation of oatmeal. Major weight loss in thermogram of oatmeal can be attributed to second region (225–465˚C) which is around 67%.

In case of OAT-g-PMMA-5, first region (20–207˚C) is due to loss of moisture. The second (207–343˚C) and third zone (343–467˚C) are associated with degradation and combustion of main backbone of oatmeal. A fourth zone (467–645˚C) of weight loss is due to degradation of grafted PMMA chains which overlaps with the third zone of weight loss of oatmeal backbone and the fifth zone (645–794˚C) refers to complete degradation of grafted biopolymer. The comparative TGA curves of oatmeal and OAT-g-PMMA-5 has been depicted in Fig. 4.

3.2.6. Number-average MW of the polymers

The number-average MW is calculated using the following equation

$$\frac{\rho}{C_{\mathrm{dry}}} = \frac{\Phi \times n}{M_n} \times 10^3 \tag{7}$$

where M_n is the number-average MW, C_{dry} is the concentration of the dry sample in the solution, Φ is the osmotic coefficient, which accounts for the non-ideal behaviour of the solution (here, assuming that the

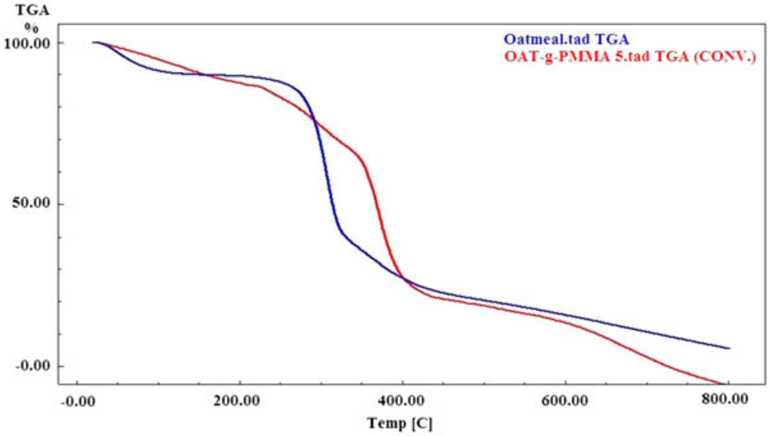

Fig. 4. Combined TGA curve of oatmeal and OAT-g-PMMA-5.

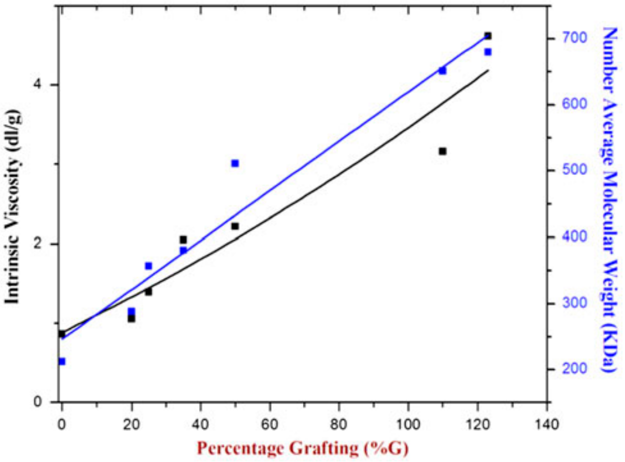

Fig. 5. Relationship of intrinsic viscosity, percentage grafting and number-average MW of oatmeal and various grades of OAT-g-PMMA.

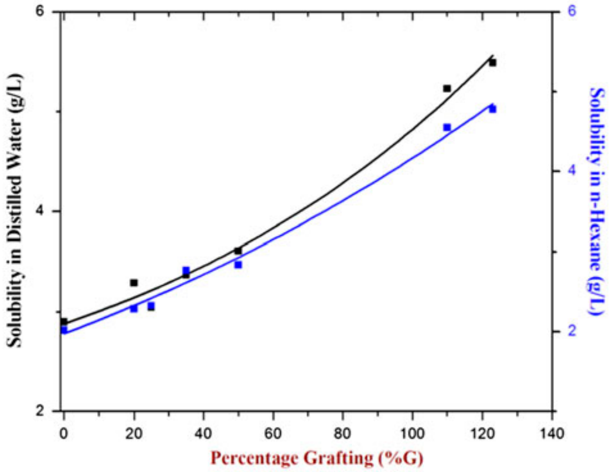

Fig. 6. Solubility scheme of oatmeal and different grades of OAT-g-PMMA in polar and non-polar solvents.

sample behaves ideally), n is the number of components into which a molecule dissociates and ρ is the osmosis per kilogram solvent [65]. As evident from Table 1, higher the percentage grafting, higher is the number-average MW. This is due to the greater number of methyl methacrylate monomers grafted. The correlation between the three parameters i.e. percentage grafting (%G), intrinsic viscosity and number-average MW is depicted in Fig. 5.

3.2.7. Solubility in polar and non-polar solvent

The solubility of oatmeal and different grades of OAT-g-PMMA in polar and non-polar solvent have been graphically presented in Fig. 6. All the grades of grafted oatmeal have shown better solubility than starting biopolymer (oatmeal). Solubility in polar solvent is found to be somewhat superior to solubility in non-polar solvent. Since oatmeal has an amphiphilic polysaccharide and protein part, it shows partial solubility in both types of solvents i.e. polar (e.g. aqueous solution) as well as non-polar (e.g. n-hexane). Grafting of polar monomers (i.e. methyl methacrylate) on the backbone of oatmeal has improved solubility by virtue of incorporated polar groups. Subsequently, higher the percentage grafting of the oatmeal, higher is the solubility in aqueous solution in contrast with solubility in n-hexane i.e. the best grade (the grade with highest percentage grafting) has highest solubility in both type of solvents.

3.2.8. Zeta potential measurement

Theory and principle of zeta potential states that the stability of suspension increases due to higher zeta potential as a result of aggregation of charged particles. Zeta potential of 0.25 wt.% kaolin suspension using blank (without flocculant), optimized best dosage of parent biopolymer i.e. oatmeal (1.28 ppm) and optimized best grade and dosage of OAT-g-PMMA (i.e. grade 5) were determined in aqueous solution at variable pH (i.e. pH 7, 10 and 4) the comparative graph of zeta potential at variable pH in 0.25% kaolin is represented in Fig. 7 and values are tabulated in Table 3. The results evident that grafted biopolymers show higher zeta potential in 0.25 wt.% kaolin Suspension compared to starting biopolymer as well as blank suspension having the most inferior zeta potential value.

3.2.9. ^{13}C-CP/MAS solid-state NMR spectroscopy

^{13}C-CP/MAS solid-state NMR spectrum of oatmeal (Fig. 8(a)) shows four distinct peaks at δ = (104.064, 102.636, 101.537 and 100.438 ppm). These peaks have identical chemical environment and can be assigned to anomeric C-atom (i.e. C-1 in six-membered ring), peak at δ = 83.075 ppm is due to the C-atoms connected to –OH groups in the moiety i.e. C-2, C-3 and C-4 atoms, peak at δ = 73.514 ppm for C-atom of $–CH_2OH$ group and finally peak at δ = 63.294 ppm may be considered for the C-5 C-atom present at six-membered ring in oatmeal [41].

^{13}C-CP/MAS solid-state NMR Spectrum of OAT-g-PMMA-5 (Fig. 8(b)), discloses many supplementary peaks at δ = 184.397 ppm which may be considered for ester carbonyl C-atom [66], peaks at δ = 58.459 ppm for $(–CH_2–)$ C-atom which has been hybridized from sp2 to sp3 C-atom due to polymerization reaction [67,68], peaks at δ = 22.743 ppm stands for α-CH_3 C-atom and peak at δ = 51.535 ppm for quaternary C-atom. The above peaks mentioned are present in OAT-g-PMMA-5 in contrast with ^{13}C-SSNMR peaks of parent biopolymer i.e. pure oatmeal which essentially confirms the grafting of MMA on the backbone of parent biopolymer i.e. oatmeal. The δ value for OAT-g-PMMA-5 is slightly shifted for C-1–C-5 C-atom and C-6 C-atom for $–CH_2OH$ of oatmeal due to the grafting.

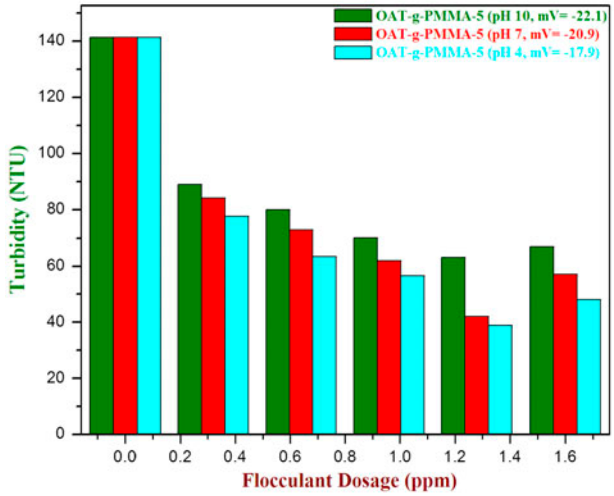

Fig. 7. Comparative graph of zeta potential at variable pH (i.e. 7, 4 and 10) using blank and OAT-g-PMMA-5.

3.2.10. Powder X-ray diffraction

The outcome of P-XRD analysis of oatmeal and representative OAT-g-PMMA-5 has been revealed in Fig. 9(a) and (b), respectively. From the obtained peak of parent biopolymer i.e. oatmeal (Fig. 9(a)), it can be observed that it has more intense peaks than that of grafted biopolymer i.e. OAT-g-PMMA-5 (Fig. 9(b)). This suggests the amorphous nature of oatmeal has been increased due to the grafting reaction on its backbone. The amorphous materials generally have higher water solubility. Successful grafting led to an increase in amorphous nature of modified oatmeal and this was reflected by the solubility of oatmeal and various synthesized grades of grafted biopolymer as reported in Fig. 5 and Table 1.

3.3. Flocculation characteristics in kaolin suspension and municipal wastewater

The overall performance of synthesized grade of grafted biopolymer, parent biopolymer (oatmeal) and alum as flocculants for 0.25 wt.% kaolin suspensions has been investigated. All the grades of grafted oatmeal have shown better flocculation efficacy than oatmeal and alum as expected. This is due to the higher hydrodynamic volume (i.e. intrinsic viscosity) of the macromolecule as given in Table 1, results in its superior flocculation efficacy [69]. There is a direct correlation witnessed for all grade of OAT-g-PMMA. Higher the intrinsic viscosity, higher is the percentage grafting, and higher the percentage grafting, higher is the flocculation efficacy.

The flocculation study in 0.25 wt.% kaolin suspensions (using standard "jar test" protocol) for dosage varying between 0 ppm (control) and 1.6 ppm has been revealed in Fig. 10a. Evidently, among the various grades of OAT-g-PMMA, the optimized grade

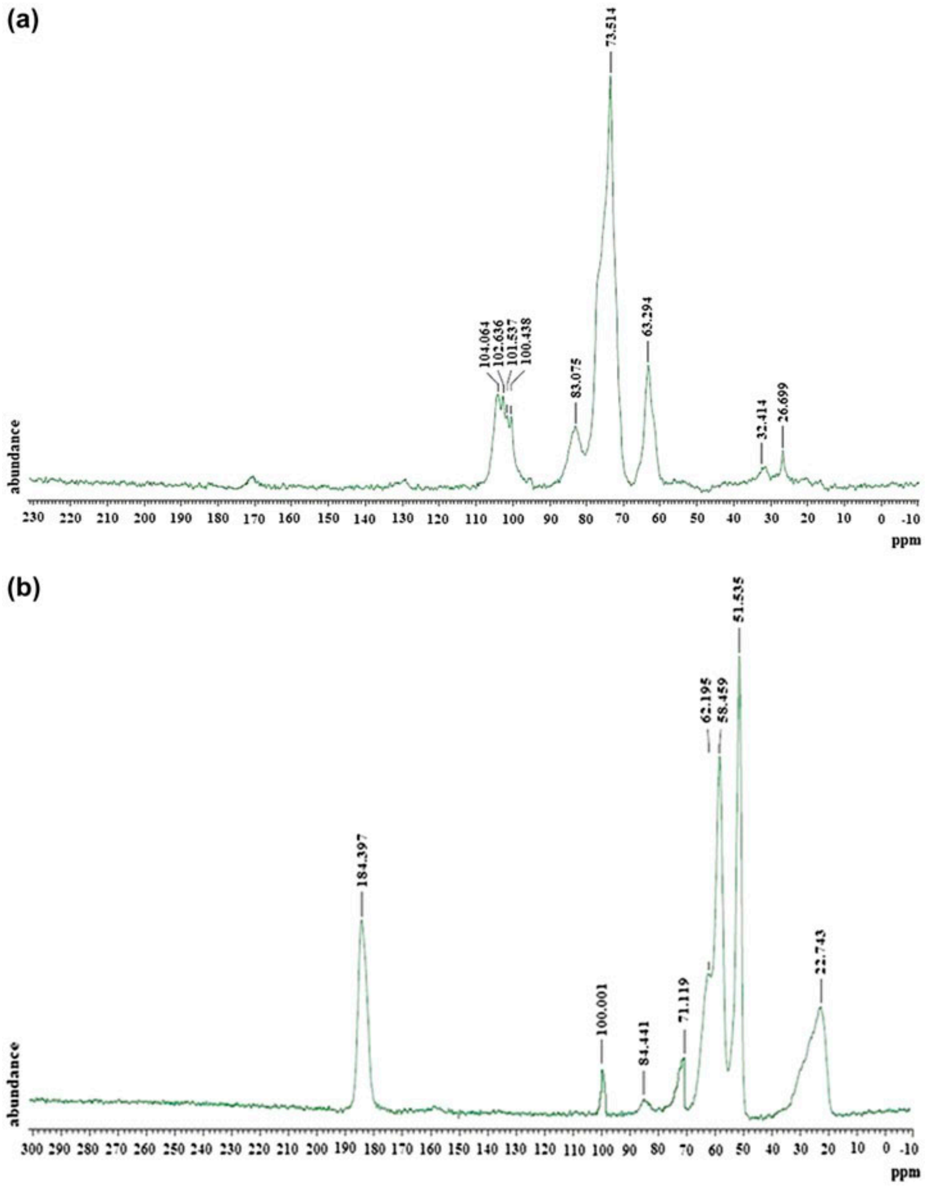

Fig. 8. ^{13}C-CP/MAS solid-state NMR Spectroscopy of (a) oatmeal and (b) OAT-g-PMMA-5.

(OAT-g-PMMA-5) showed maximum flocculation efficacy due to its highest hydrodynamic volume (i.e. intrinsic viscosity). This further confirms the extension of Singh's easy approachability model [17,70] for the grafted PMMA systems also. For all the polymers studied and applied as flocculant, there is an optimal dosage at which the flocculation efficacy is maximum, beyond which the flocculation decreases. This behaviour of the flocculation curve finely confirms the *bridging mechanism* [71].

The settling tests were carried out in 0.25 wt.% kaolin suspension. In this case, the settling time was plotted against the height of interface. Fig. 10c shows the settling characteristics in kaolin suspension for oatmeal and different grades of OAT-g-PMMA. In absolute concurrence with the "jar test" protocol above, OAT-g-PMMA-5 has the highest settling rate. Moreover, the settling rate of the various grades follows the same order as in "jar test" consequence i.e. higher the percentage grafting, higher is the settling rate. The settling rate is a reliable indicator of flocculation efficacy. The higher the settling rate of the floc-containing contaminants better will be its flocculation performance. From the settling curve (Fig. 10c), it is observed that

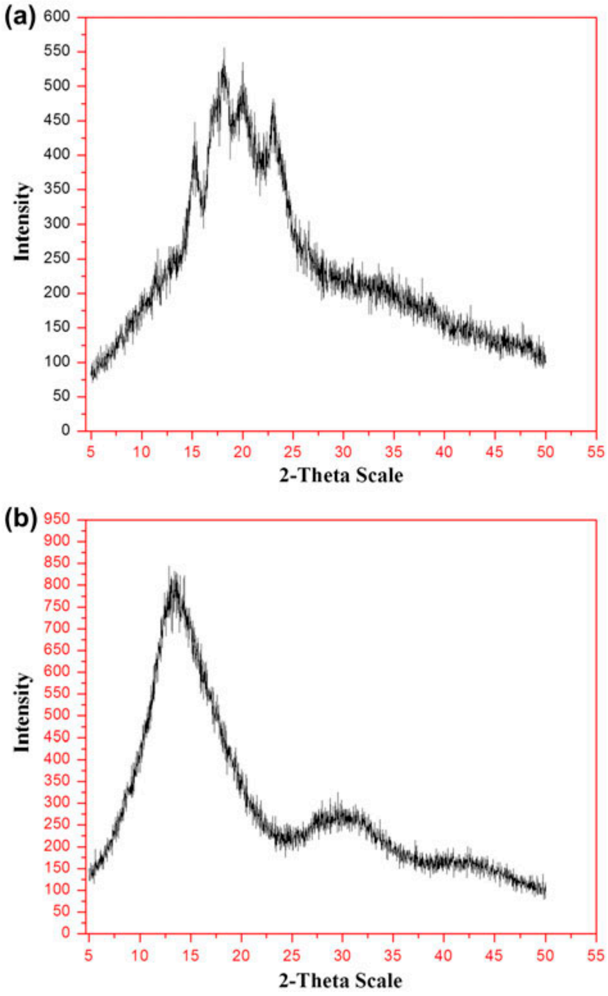

Fig. 9. Powder X-ray diffraction measurements of (a) oatmeal and (b) OAT-g-PMMA-5.

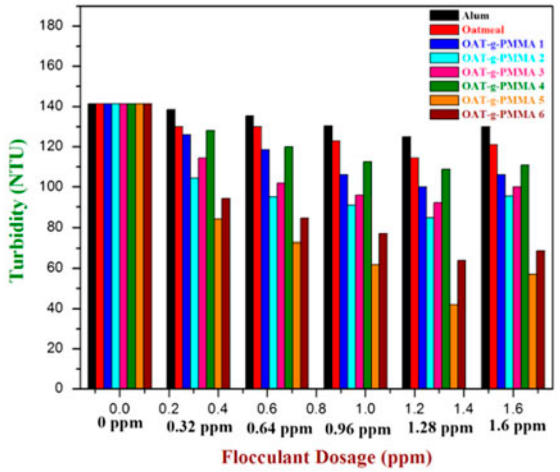

Fig. 10a. Flocculation profile in kaolin suspension.

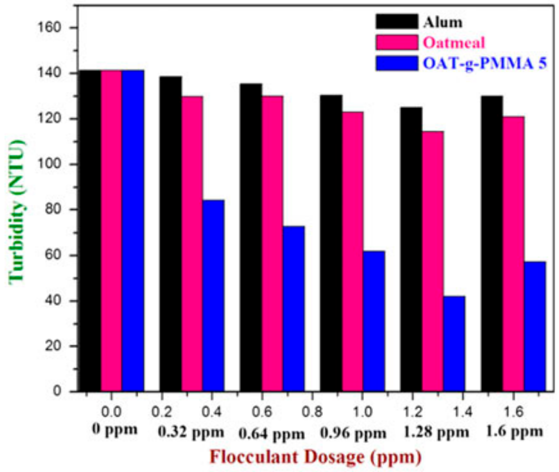

Fig. 10b. Comparative flocculation profile of alum, oatmeal and OAT-g-PMMA-5 in 0.25 wt.% kaolin suspension.

the fall of the interface is linear for a considerable height before it becomes non-linear. This means that initially the rate of fall of the interface is constant, after which it gradually declines. From Brostow, Pal and Singh model of flocculation, radius of gyration is directly proportional to settling rate [70]. In this case, higher the percentage grafting, higher is the hydrodynamic volume/radius of gyration of the flocculant molecule, hence higher is the settling rate.

The optimal dosage of OAT-g-PMMA-5 as flocculant is 1.28 ppm. In other words, the dosage translates to the fact that 1 kg of OAT-g-PMMA-5 can be used for treatment of 7, 81,250 L of effluent discharged from municipal wastewater.

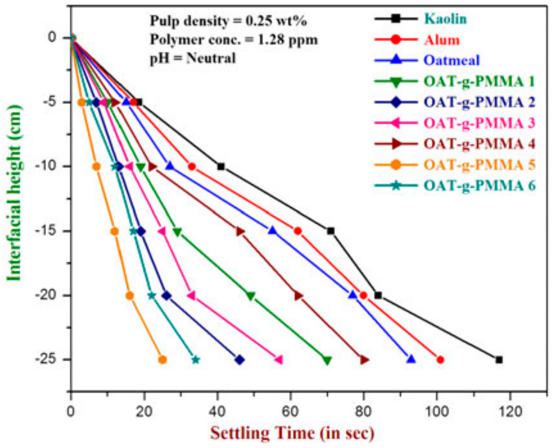

Fig. 10c. Settling profile of parent biopolymer (oatmeal) & various grades of OAT-g-PMMA in 0.25 wt.% kaolin suspension.

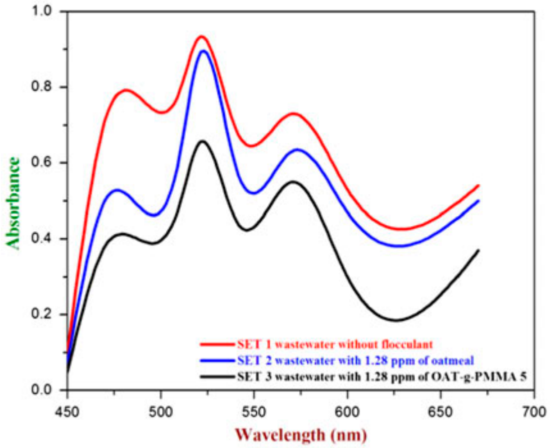

Fig. 10d. Colour removal profile in municipal wastewater.

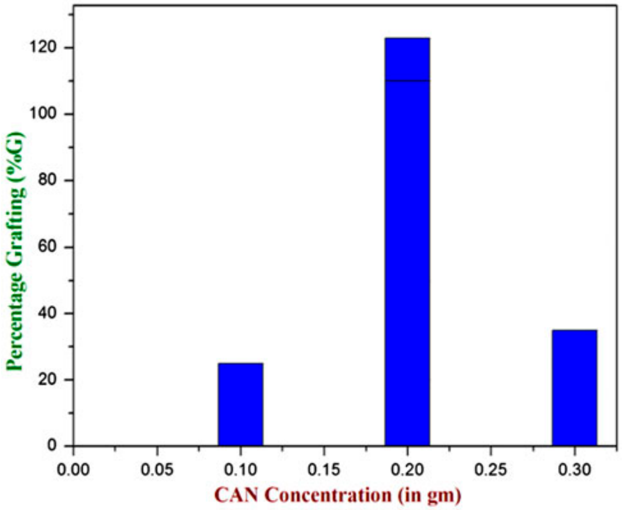

Fig. 11. Effect of initiator (CAN) concentration over percentage grafting (%G).

OAT-g-PMMA-5 was found to considerably reduce the pollutant load in the wastewater effluent, as witnessed by analysis of supernatants drawn from the "jar test" protocol at optimized flocculant dosage (1.28 ppm).

A comparative study of water quality of supernatants Table 4 from "jar test" protocol in case of municipal wastewater (SET 1), municipal wastewater with 1.28 ppm of oatmeal as flocculant (SET 2) and municipal wastewater with 1.28 ppm of OAT-g-PMMA-5 as flocculant (SET 3) have shown excellent water quality. Drastic reduction in metal content (Cr, Fe, Mn and Ni) and appreciable diminution in organic load (in terms of BOD_5 and COD) were observed. Suspended particles (TS, TDS and TSS) and turbidity concentrations were also drastically reduced. An impressive performance in removal of colour was also noted Fig. 10d.

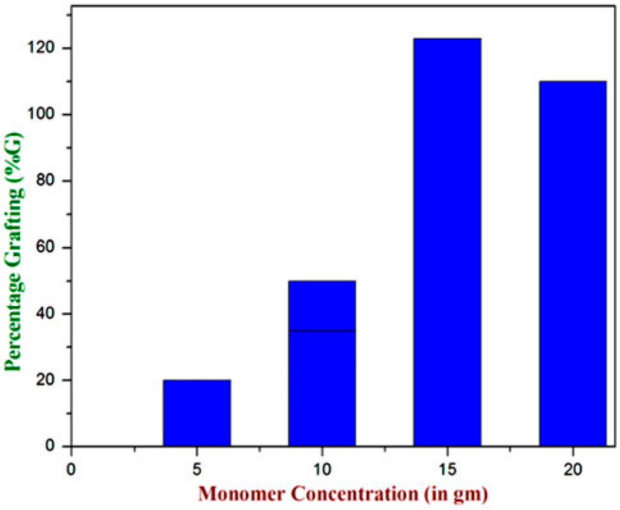

Fig. 12. Effect of monomer (MMA) concentration over percentage grafting (%G).

From Figs. 10a and 10b the dismayed performance of alum in treating the kaolin suspension at the dosage under study was observed.

4. Conclusions

Polymethyl methacrylate-grafted oatmeal (OAT-g-PMMA) is synthesized by "conventional" technique involving CAN to commence the free radical graft copolymerization reaction. The synthesized grades of novel graft copolymers were characterized through various physicochemical techniques. Further, it has been assessed for its potential application in municipal wastewater treatment through standard "jar test" protocol. OAT-g-PMMA-5 (i.e. best grade) showed the maximum flocculation efficacy compared to oatmeal and alum. It proves that OAT-g-PMMA-5 is an efficient flocculant than both starting material and alum for the treatment of effluents discharged from municipal wastewater. The higher flocculation efficacy of the grafted product than the parent biopolymer is also in accordance with Brostow, Pal & Singh model of flocculation as well as "Singh"s easy approachability model'. The optimized dosage of flocculation for OAT-g-PMMA has been found to be 1.28 ppm.

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