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Synthesis, Characterization and Application of Polymethyl Methacrylate Grafted oatmeal: A potential Flocculant for Wastewater Treatment

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ABSTRACT: The studies report the synthesis of novel graft copolymer of oatmeal. Polymethyl methacrylate grafting was carried out on oatmeal backbone via 'microwave assisted' approach. The graft copolymers were optimized by varying monomer and CAN concentration. The synthesized graft copolymers were characterized by intrinsic viscosity, FTIR, TGA, SEM, Elemental Analysis, number average molecular weight and solubility. All the grades of graft copolymers were assessed for its potential application as a flocculant in 1 wt% coal-fine suspension, 0.25 wt% kaolin suspension and municipal wastewater using standard 'jar test' protocol. The flocculation efficacy of synthesized graft copolymers was compared with commercially available coagulant (alum) in 1 wt% coal-fine and 0.25 wt% kaolin suspensions and was found to exhibit better potential as a flocculant than alum and oatmeal. Among diverse grades of graft copolymers, OAT-g-PMMA-5 exhibits higher percentage grafting, intrinsic viscosity and flocculation efficacy for removal of heavy metal ions, suspended particles and organic loads from wastewater.

Key words: Microwave assisted approach, Graft copolymers, Flocculant, Standard 'jar test' protocol, Municipal wastewater treatment

INTRODUCTION

In order to meet the local and global demands of water, the recycling of water is being practiced all over the world (Hirani et al., 2013). Wastewater is treated physically, chemically and biologically in wastewater treatment plants in order to eliminate or reduce contaminants before the release of environmentally safe water (Hong 2009; Liu 2013). Therefore, with the introduction of stringent regulations for environmental protection, proper treatment, disposal of wastewater sludge has become mandatory for any municipal and industrial installation. (Zhao et al., 2003). Dissolved organic matter (DOM) plays an important role in both natural and wastewater system (Borisover 2009; Ishii 2012; Coble 2007; Murphy 2008; Stedmon 2007; Meng 2013). Increased concentration of dissolved organic matter (DOM) due to anthropogenic activities has recently become a growing concern for drinking water treatment as well as municipal wastewater reclamation (Liu 2012; Shah 2012; Westerhoff 2002; Chon 2013; Pal 2006).

Recently water soluble graft copolymers of high molecular weight are being increasingly applied for wastewater treatment using flocculation processes. Grafting on polymeric backbone is an approach for altering the attributes of natural and synthetic polymers. Synthetic polymers are preferred than the natural ones due to their higher molecular weight, highly branched structure and high potential to adsorb the suspended particles in wastewater (Barkert et al., 1988).

Flocculation has been practised in different ways either as standalone treatment or in conjunction with coagulation-flocculation to achieve the desired water quality parameters (Rath 1998; Tripathy 2001; Pal 2005; Nayak 2001; Sen 2011; Lee 1998; Pal 2011). The flocculants might be chemical, synthetic or graft copolymers. Presently many contemporary workers have reported superior characteristics of graft copolymers over natural flocculants (Mishra 2012; Bharti 2013; Mishra 2011; Rani 2012; Sinha 2013; Thakur 2012; Mishra 2011; Mishra 2014; Rahul 2014; Rahul 2014). This study reports the development of an unexplored oatmeal based material and its potential applications for municipal wastewater treatment.

Synthesis of graft copolymers (Odian 2002; Gowariker 1986) essentially involves a free radical mechanism. The free radicals can be generated in a variety of ways. The most effective approach employs microwave irradiation alone referred as 'microwave initiated' approach or MW radiation along with chemical free radical initiator 'microwave assisted' approach (Mishra et al., 2011).

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Oatmeal is a viscous biopolymer made from Beta-D-glucan which is a soluble fibre of monosaccharide d-glucose. This means the bonds between the d-glucose or d-glucopyranosyl units are either β-1→3 linkages or β-1→4 linkages. The (1→3)-linkage breaks up the uniform structure of the betrma-d-glucan molecule and makes it soluble and flexible (Singh et al., 2013). Oatmeal contains Avenalin as a major storage protein while Prolamine and avenin are minor proteins. Oatmeal has not been altered with polymethyl methacrylate (PMMA) as graft copolymer via 'microwave assisted' approach to the best of our knowledge. In this research work we have suitably altered this natural biopolymer towards its utilization as a potential flocculant for municipal wastewater treatment.

The investigation discussed in this paper involves the synthesis of graft chains of polymethyl methacrylate (PMMA) on the backbone of oatmeal, thus resulting in formation of polymethyl methacrylate grafted oatmeal (OAT-g-PMMA). The synthesis has been carried out using 'microwave assisted' approach involving a synergism of microwave radiation (700 watts) along with ceric ammonium nitrate to initiate the grafting reaction. The flocculation efficacy of the grafted product was investigated in 1 wt% coal-fine suspension, 0.25 wt% kaolin suspensions and municipal wastewater for pollutant load diminution in terms of suspended particles, heavy metal ions and organic load present in the sample of municipal wastewater.

MATERIALS & METHODS

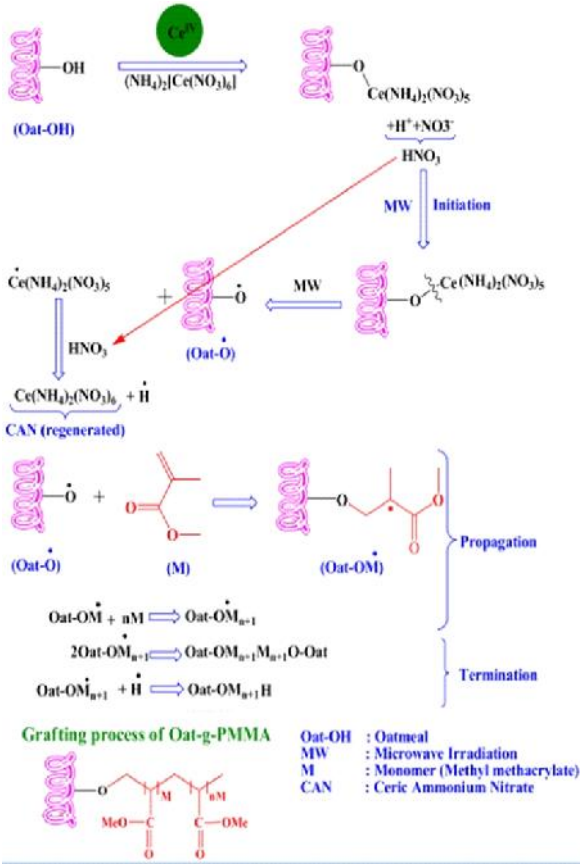
Oatmeal was obtained from Shanti food chem. Pvt. Ltd., Rajkot, Gujarat, India. Methyl methacrylate was supplied by CDH, New Delhi, India. Ceric ammonium nitrate was supplied by E. Merck (India), Mumbai, India. Acetone was purchased from Rankem, New Delhi, India. All the chemicals were used as received; without further purification.The municipal wastewater was collected from the main sewage system of Birla Institute of Technology, Mesra (BIT-Mesra) community.

A suspension of 1 g of oatmeal in 40 ml of distilled water was prepared. Required amount of methyl methacrylate was added to the oatmeal suspension. Ceric ammonium nitrate (CAN) was added to it and the suspension was subjected to microwave irradiation (Catalyst TM systems CATA 4 R) for 3 minutes, keeping the irradiation cut-off temperature at 70°C. After the stipulated time of MW irradiation excess of acetone was poured into gelatinous product and washed till constant weight was obtained. This was kept for 24 h (Kongparakul et al., 2008). This was done to minimise the probability of competing homopolymer formation reaction. The precipitated graft copolymer was recovered by decantation 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 (%G) and percentage grafting efficiency (%GE) were evaluated as:

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

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

The mechanism of synthesis of the graft copolymer has been summarized in Scheme 1.



Scheme 1: Schematic representation of mechanism for '*microwave assisted*' synthesis of OAT-g-PMMA

Viscosity measurements of the polymeric solutions were carried out with an Ubbelohde viscometer (capillary diameter 0.46mm) 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% & 0.0125%). From the time of flow of polymer solutions (t) and that of the solvent (t_0, for distilled water), relative viscosity ($\eta_{rel} = t/t_0$) was obtained. Specific viscosity

was calculated from the relation $\eta_{sp} = \eta_{rel}-1$. Subsequently, the reduced viscosity (η_{sp}/C) and the inherent viscosity ($\ln \eta_{rel}/C$) were calculated ('C' is the polymer concentration in g/dL).

Subsequently, the reduced viscosity (η_{red}) and the inherent viscosity (η_{inh}) were simultaneously plotted against concentration and the plots extrapolated to 'Y axis' to get the significance of intrinsic viscosity (Collins et al., 1973). The intrinsic viscosity thus evaluated for diverse grades of OAT-g-PMMA graft copolymer has been reported in Table 1.

The elemental analysis of oatmeal and best grade of OAT-g-PMMA (i.e. grade-5) was carried out with an Elemental Analyzer (Model: M/s Elemental, Germany; Vario EL III). The estimation of five elements, i.e. carbon, hydrogen, nitrogen, oxygen and sulphur were undertaken. The results have been tabulated in Table 2.

The FTIR spectra of oatmeal Fig. 1(a) and OAT-g-PMMA-5 Fig. 1(b) were recorded in solid state, by KBr pellet procedure with a FTIR spectrophotometer. (Model: IR-Prestige 21, Shimadzu Corporation, Japan) between 400 and 4000/cm.

A comparative thermo gravimetric analysis (TGA) of oatmeal and OAT-g-PMMA-5 was carried out with TGA instrument (Model: DTG-60; Shimzadu, Japan).The study was performed in an inert atmosphere (nitrogen) from 25°C to 800°C. The heating rate was uniform in all cases at 5°/min. The TGA curve for oatmeal, OAT-g-PMMA-5 and comparative are plotted in Fig. 2(a), Fig. 2(b) and Fig. 2(c) respectively.

Scanning Electron Microscopy (SEM) of oatmeal Fig. 3(a) and OAT-g-PMMA-5 Fig. 3(b) was carried out in powdered form (Model: JSM-6390LV, Jeol, Japan). Samples were coated with a thin layer of platinum with the help of platinum coater [JEOL Auto fine coater model: JFC-1600 auto fine coater, with coating time of 120 sec with 20mA]. The micrographs of these samples were recorded at various magnifications.

The number average molecular weight of oatmeal and various grades of OAT-g-PMMA were estimated in aqueous solvent (distilled water) by Osmometry (A+Adv. Instruments, INC. Model: 3320, Osmometer). Data representing the number average molecular weight of oatmeal and various grades of OAT-g-PMMA are tabulated in Table 1.

Solubility of oatmeal and various grades of OAT-g-PMMA were estimated via standard gravimetric process at room temperature (25°C) in polar (distilled water) and non-polar (n-Hexane) solvents separately. Data representing solubility values of oatmeal and various grades of OAT-g-PMMA are tabulated in Table 1.

Concentration of various metals in municipal wastewater collected from BIT-Mesra Community, were determined by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES), Model: Optima 2100DV, Perkin Elmer, USA and reports has been tabulated in Table 3.

OAT-g-PMMA was used as a flocculant for 1 wt% coal-fine suspension, 0.25 wt% kaolin suspension and municipal wastewater (collected from BIT-Mesra). 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(R) beaker. Calculated amount of the flocculant (oatmeal or various grades of OAT-g-PMMA) or coagulant (alum) was added in concentrated solution form (in case of blank no flocculant was added) to achieve the optimize dose. The solutions were identically stirred in 'jar test' apparatus, at 150 r.p.m for 30 seconds, 60 r.p.m for 5 minutes, followed by settling time of 5 min (Héctor et al., 2011). Afterwards, supernatant liquid was collected using pipette and optical density was measured for coal fine suspension in a calibrated spectrophotometer (ELICO® double beam SL 210 UV-VIS Spectrophotometer) at λmax 520 nm. For kaolin suspension the settling time was followed by 15 min, and turbidity of supernatant was measured in nephelo-turbidity meter (Digital Nephelo-Turbidity Meter 132, Systronics, India). The flocculation efficacy thus studied for oatmeal and various grades of OAT-g-PMMA and alum have been graphically compared in Fig. 4(a) (for coal-fine suspension) and Fig. 4(b) (for kaolin suspension). Flocculation curves of OAT-g-PMMA-5 (Best Grade) with respect to oatmeal and alum has been graphically compared and represented in Fig. 4(c) and Fig. 4(d) for coal-fine and kaolin suspension respectively. Similarly, the flocculation experiments were carried out for municipal wastewater in triplicate, without flocculant, with optimized dosage (0.8 ppm) of oatmeal and OAT-g-PMMA-5 as optimized from coal-fine and kaolin suspension flocculation performance.

The experiment was done in three sets as follows:

SET 1: municipal wastewater without flocculant

SET 2: municipal wastewater with 0.8 ppm of oatmeal

SET 3: municipal wastewater with 0.8 ppm of OAT-g-PMMA-5

The water quality of these supernatants was analysed by standard procedures (Greenberg et al., 1999), as reported in Table 3.

RESULTS & DISCUSSION

This procedure is a hybrid of 'microwave initiated' and 'conventional' method of synthesis i.e., it is based on free radical mechanism using microwave radiation

(700 watts) along with ceric ammonium nitrate to generate free radical sites on the oatmeal backbone. A series of graft copolymers were synthesized by varying CAN and methyl methacrylate 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 increases with increase in molecular weight as apparent from Table 1. The synthesis 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); and then w.r.to methyl methacrylate keeping other factors constant (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 weight of 15 g and CAN concentration of 0.2 gm in the reaction mixture (~ 40 ml), when the microwave power is maintained at 700 watts.

In the crystal structure of CAN, Ceric ion is surrounded by oxygen atoms from six-bidentate nitrate ions resulting in a 12-coordinate icosahedral geometry (Greenwood et al., 1997). Cerium (IV) takes electrons from C-6 alcoholic oxygen in oatmeal to form a new Ce-O bond that is predominately ionic in character, owing to its large size. This new bond being more polar than O-H, cleaves readily in the presence of microwave irradiation. The process results in generation of free radical sites on the backbone of oatmeal, where the graft chains are attached. The proposed mechanism of 'microwave assisted' synthesis has been proposed in various studies (Mishra 2011; Rani 2012; Mishra 2014). The proposed mechanism of 'microwave assisted' synthesis is illustrated in Scheme 1 (Bharti 2015; Mishra 2011; Mishra 2014).

As evident from Table 1, intrinsic viscosities of all grades of OAT-g-PMMA are greater than that of oatmeal confirming the grafting process. This is due to increase in the hydrodynamic volume resulting from grafting of 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 relation-ship (intrinsic viscosity $\eta = KM^{\alpha}$, where K and α are constants, both related to stiffness of the polymer chains). Hence, increase in intrinsic viscosity is due to increase in molecular weight (M) as a result of grafting. The values correlating intrinsic viscosities with their concerned percentage grafting is tabulated in Table 1.

The results of elemental analysis for oatmeal, polymethyl methacrylate (PMMA) and that of the best grade of polymethyl methacrylate grafted oatmeal (OAT-g-PMMA-5) are given in Table 2. The data clearly

Table 1. Synthesis detail of OAT-g-PMMA via '*microwave assisted*' approach

Polymer Grade	Wt. of oatmeal	Wt. of methyl methacrylate	Wt. of CAN	Time of irradiation	% grafting	% grafting efficiency	Intrinsic viscosity	Number average molecular weight (kDa)	Solubility (gm/L)	
									In H2O	In n-Hexane
	(gm)	(gm)	(gm)	(sec)	(% G)	(%GE)	(dl/g)			
OAT-g-PMMA-1	1	10	0.1	180	28	2.8	3.22	410	3.19	3.01
OAT-g-PMMA-2	1	10	0.2	180	55	5.5	3.5	585	4.74	3.74
OAT-g-PMMA-3	1	10	0.3	180	40	4	3.4	451	4.11	3.31
OAT-g-PMMA-4	1	5	0.2	180	22	4.4	3.09	312	3.12	2.94
OAT-g-PMMA-5	**1**	**15**	**0.2**	**180**	**130**	**8.66**	**6.25**	**713**	**7.99**	**6.54**
OAT-g-PMMA-6	1	20	0.2	180	122	6.1	6.02	692	7.84	6.23
Oatmeal (OAT)	-	-	-	-	-	-	0.7	212	2.9	2.02

Table 2. Elemental contents of PMMA, Oatmeal and OAT-g-PMMA-5

Polymer grade	%C	%H	%N	%O	%S
PMMA	60.59	7.12	0.000	32.29	0.000
Oatmeal	43.58	8.47	2.192	45.47	0.297
OAT-g-PMMA-5	48.86	8.10	1.84	41.02	0.18

shows that the grafted product has an elemental composition which is intermediate of its constituents OAT and PMMA.

As evident from Fig. 1(a), OAT has two O-H stretching peaks at 3759.26/cm and 3560.59/cm, which are due to stretching vibration of -OH (-CH_2OH). One peak at 3275.13/cm can be attributed to N-H stretching vibration due to the presence of protein chain in oatmeal. Peaks at 2927.92/cm and 2856.58/cm are assigned to the C-H stretching vibrations. The Peak at 1745.58/cm is due to C=O stretching vibrations, N-H bending peak at 1662.64/cm and C-N stretching peaks are evident at 1338.60/cm.

From Fig. 1(b) it is clear that all the above peaks present in oatmeal are also present in OAT-g-PMMA-5 excluding the peaks pertaining to O-H stretching vibrations.ed The peaks 3759.26/cm, and 3560.59/cm, for O-H stretching vibration present in case of oatmeal has not been found in OAT-g-PMMA-5; thus confirming the grafting. The concerned spectrums are shown in Fig. 1(a)-Fig. 1(b).

In case of oatmeal, three distinct zones of weight loss are observed Fig. 2(a)-Fig. 2(b). 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 thermo gram of oatmeal can be attributed to third region (465-800°C).

In case of OAT-g-PMMA-5, first region (18-222°C) is due to loss of moisture. The second (222-346°C) and third zone (346-430°C) correspond to the degradation and combustion of main backbone of oatmeal. A fourth zone (430-618°C) of weight loss due to degradation of grafted PMMA chains which overlaps the third zone of weight loss of OAT backbone and the fifth zone (618-800°C) refers to complete degradation of biopolymer. From the comparative TGA curves of OAT and OAT-g-PMMA-5 Fig. 2(c), it is clear that the grafted product is more stable as compared to starting biopolymer. This further confirms the enhanced thermal stability of oatmeal due to grafted PMMA chains. The concerned spectrums of TGA are shown in Fig. 2(a)-2(c).

It is evident that profound morphological change from granular structure to fibrillar structure has taken place because of grafting of PMMA chains on the backbone of biopolymer. The concerned spectrums of SEM are shown in Fig. 3(a)-3(b).

The Number average molecular weight is calculated using the following equation

$$\frac{\pi}{C_{dry}} = \frac{\Phi \times n}{M_n} \times 10^3$$

Where, Mn is the Number average molecular weight, Cdry is the concentration of the dry sample in the solution, Φ is the osmotic coefficient, which accounts for the non ideal behavior of the solution, n is the number of components into which a molecule dissociates, π is the osmotic pressure per kilogram solvent (Sen et al., 2014; Rong et al., 2009).

As evident from Table 1, higher the percentage grafting, higher is the number average molecular weight. This is due to higher % grafting of the grafted products due to addition of monomeric moieties on to the backbone of parent biopolymer.

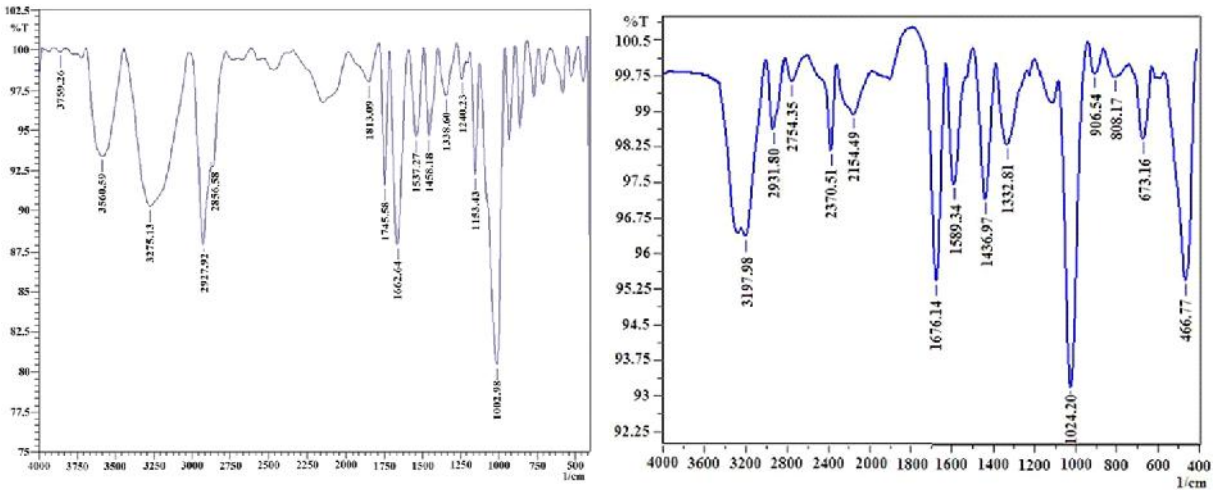


Fig. 1(a-b). FTIR spectrum of oatmeal & OAT-g-PMMA-5

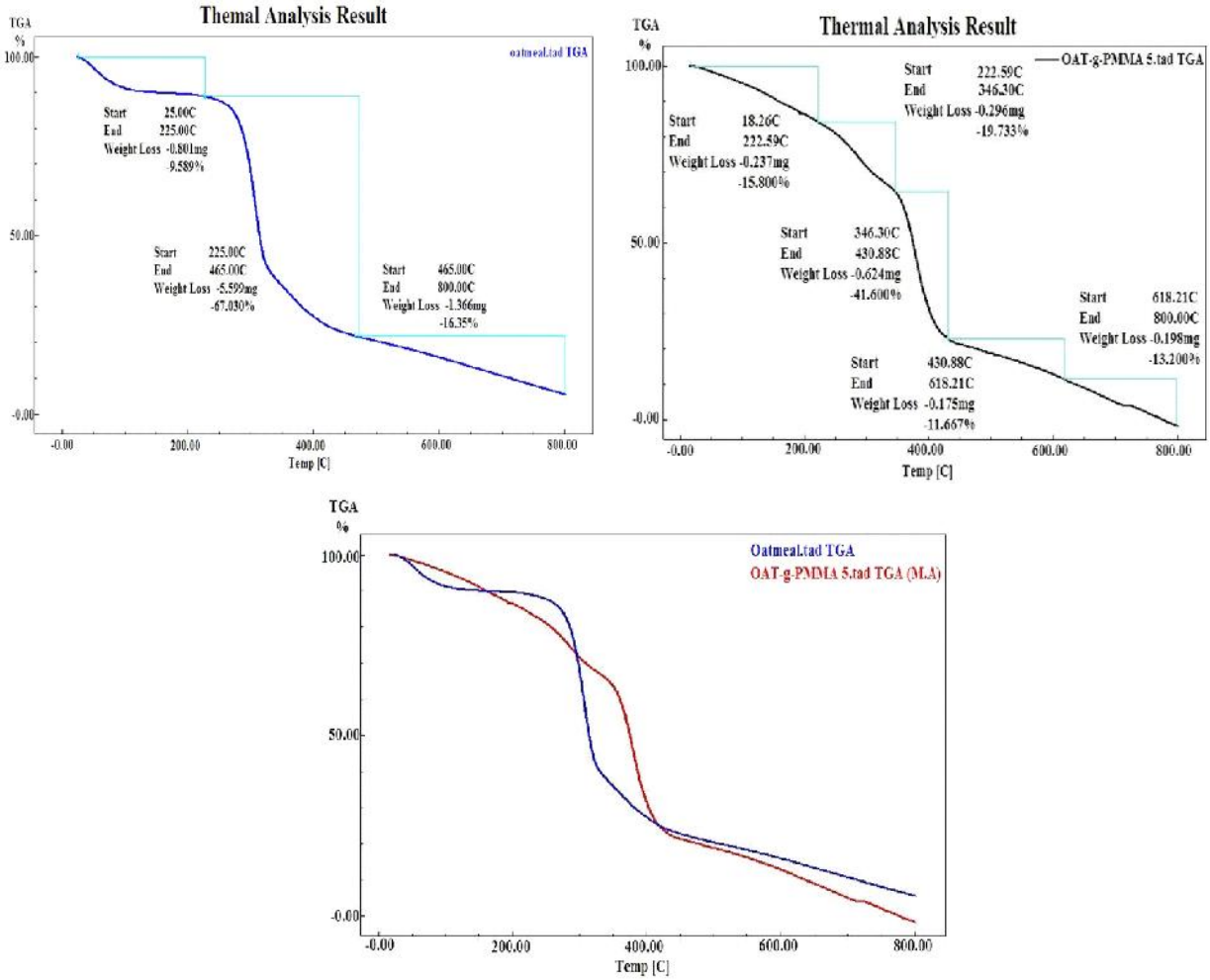


Fig. 2(a-c): TGA curve of oatmeal, OAT-g-PMMA-5 & Comparative TGA Curve of oatmeal and OAT-g-PMMA-5.

The solubility details of oatmeal and different grades of OAT-g-PMMA in polar (distilled water) solvent and non polar (n-Hexane) solvent have been tabulated Table 1. All the grades of grafted oatmeal have shown better solubility than the oatmeal. Solubility in polar solvent is found to be relatively greater than solubility in non polar solvent. Since, oatmeal contains an amphiphilic protein and polysaccharide; it shows partial solubility in both types of solvents. Grafting of polar monomers (i.e., methyl methacrylate) on the backbone of oatmeal has improved solubility by virtue of the incorporated polar groups. Consequently, the higher the percentage grafting of the oatmeal, the higher is the solubility in aqueous solution in contrast with solubility in n-hexane i.e., the best grade has highest solubility in both types of solvents.

Concentration of heavy metals like As, Cd, Cr, Fe, Mn, Ni and Pb were determined by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES), Model: Optima 2100DV, Perkin Elmer, USA. Samples of municipal wastewater were subjected to ICP-OES analysis for assessment of heavy metals present in it before and after treatment. The results are tabulated in the Table 3. It is apparent from analysis results that SET-3 i.e. wastewater treated with OAT-g-PMMA-5 shows removal of heavy metals up to a considerable extent compared to wastewater with raw material (oatmeal), thus signifying OAT-g-PMMA-5 as a potential flocculant for municipal wastewater treatment. For heavy metal contents the % removal efficiency using the best grade of synthesized flocculant varied from 51.31 % to 93.50% while Cd reduced to below detection limits (BDL). The percentage removal efficiency of heavy metal contents are tabulated in Table 3.

The flocculation characteristics of oatmeal, OAT-g-PMMA and alum have been studied in 1 wt% coal-fine suspension and 0.25 wt% kaolin suspensions using standard 'jar test' apparatus, for dosage varying between 0 ppm (control) and 1.0 ppm in Fig. 4(a)-4(d).

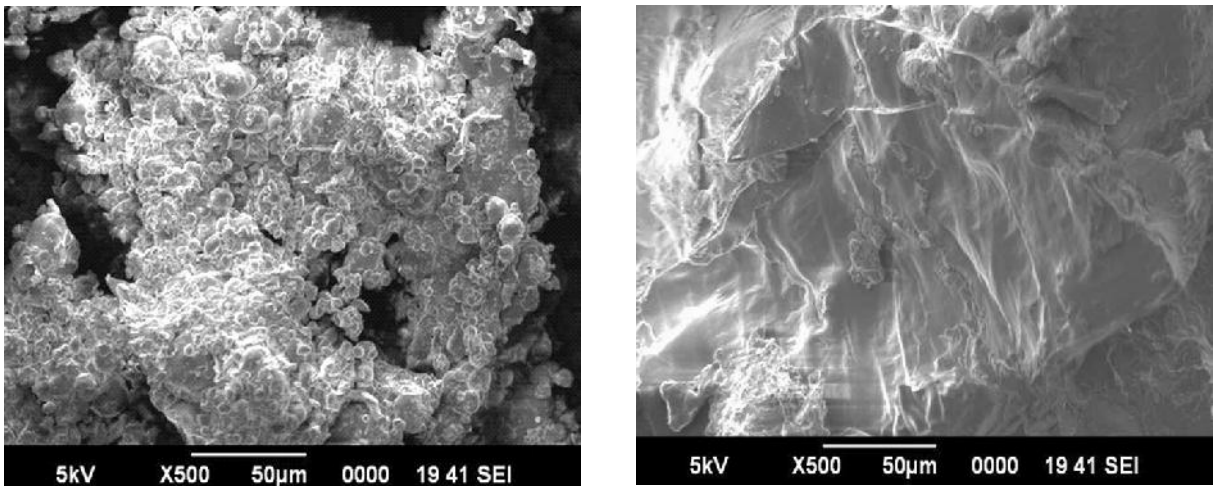


Fig. 3(a-b). SEM morphology at 500X magnification of oatmeal & OAT-g-PMMA-5

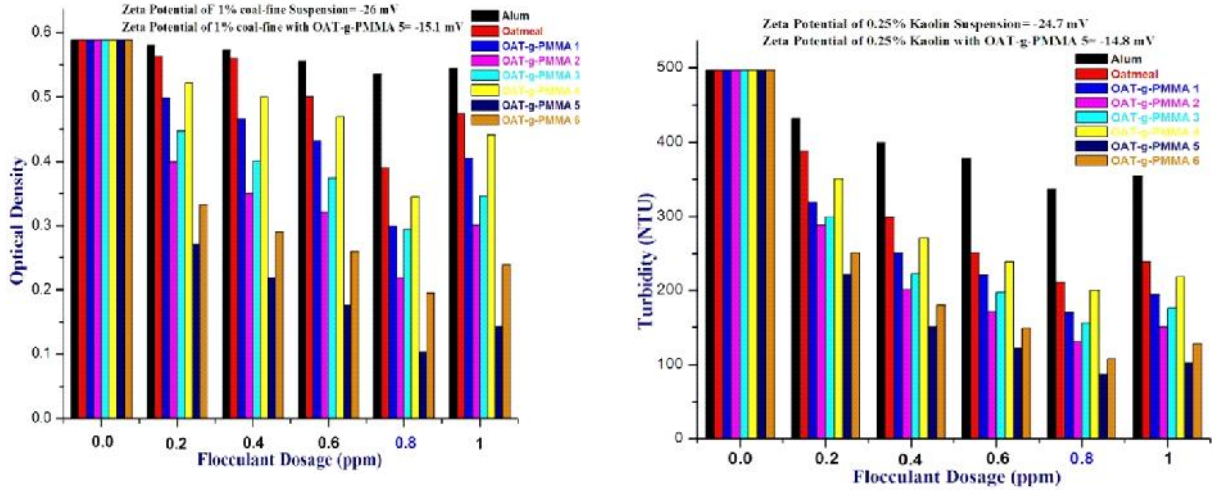


Fig. 4(a-b): Flocculation profile in 1 wt% coal-fine suspension & in 0.25 wt% kaolin suspension

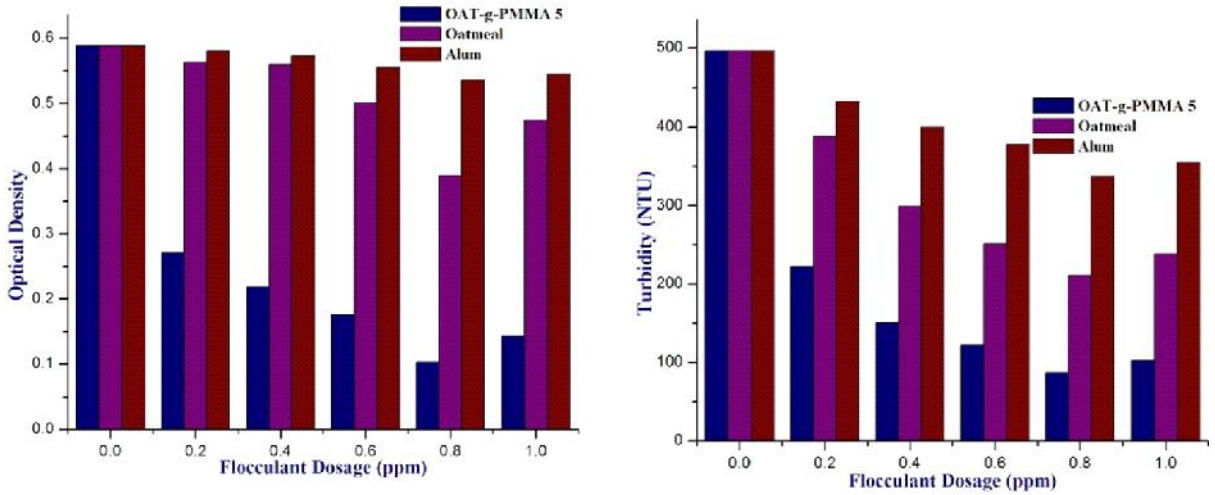


Fig. 4(c-d): Comparative flocculation curve of oatmeal, OAT-g-PMMA-5 and alum in 1 wt% coal-fine suspension & oatmeal, OAT-g-PMMA-5 and alum in 0.25 wt% kaolin suspensions

Table 3. Physicochemical properties and metal contents of treated municipal wastewater.

Turbidity (NTU)	153	104	**47**	69.28
BOD_5 (ppm)	180	137	**67**	62.77
COD (ppm)	540	468	**183**	66.11
As (ppm)	0.077	0.032	**0.005**	93.50
Cd (ppm)	0.011	0.005	**-0.003 (BDL)**	100.00
Cr (ppm)	4.08	3.03	**1.56**	61.76
Fe (ppm)	8.24	5.31	**1.44**	82.52
Mn (ppm)	0.355	0.277	**0.093**	73.80
Ni (ppm)	0.456	0.400	**0.222**	51.31
Pb (ppm)	0.089	0.071	**0.012**	86.51

CONCLUSION

Polymethyl methacrylate grafted oatmeal (OAT-g-PMMA) was synthesized via 'microwave assisted' technique, which involved a synergism of both microwave irradiation as well as ceric ammonium nitrate to initiate the free radical grafting reaction. The synthesized grades of novel graft copolymer of OAT-g-PMMA have been assessed for its potential application in water treatment through standard 'jar test' protocol. OAT-g-PMMA-5 showed the maximum flocculation efficacy compared to other grades of grafted products, oatmeal and alum as predicted by 'Brostow, Pal and Singh model of flocculation'. The higher flocculation efficacy of the grafted product is also in accordance with 'Singh's easy approachability model'. The high flocculation efficacy of PMMA grafted oatmeal, particularly OAT-g-PMMA-5 in 1 wt% coal-fine and 0.25 wt% kaolin suspensions proves it to be a superior flocculant than other grafted grades, oatmeal and alum. The optimized dosage of OAT-g-PMMA for flocculation performance has been found to be 0.8 ppm.

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