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A novel polymeric flocculant based on polyacrylamide grafted inulin: Aqueous microwave assisted synthesis

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ABSTRACT

Polyacrylamide grafted inulin (In-g-PAM) was synthesized via *aqueous microwave assisted* method (using ceric ammonium nitrate in synergism with microwave in aqueous medium). The intended grafting of the PAM chains on polysaccharide backbone was confirmed through standard physicochemical characterization techniques, namely intrinsic viscosity measurement, Fourier transform infrared (FTIR) spectroscopy, elemental analysis (C, H, N and O), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) studies. Flocculation efficacy of various grades of synthesized grafted product was studied in coal fines suspension, in relation to inulin (parent polysaccharide). This was done utilizing *jar test* and *settling test* procedure, towards possible application as a flocculant for coal washery effluents.

1. Introduction

1.1. Inulin – isolation, uses and chemical structure

Inulin is a natural and abundant, renewable polysaccharide that is found in many regularly consumed vegetables, fruits and cereals as a storage carbohydrate (Van Loo, Coussement, De Leenheer, Hoebregs, & Smits, 1995). After starch, they are the most plentiful carbohydrates occurring in plant kingdom. First isolated from the roots of *Inula helenium* (perennial herbs of *Compositae* family), inulin is industrially produced from chicory roots (*Chicorium intybus*) and Jerusalem artichoke (*Helianthus tuberosus*) (Kaur & Gupta, 2002). Dahlia (*Dahlia pinnata*) and yacon (*Smallanthus sonchifolius*) tubers are some of its other important sources.

Inulin is a nondigestible polyfructose having many diverse applications. It is widely used in food, feed, biofuels, water purification and pharmaceutical industries. In food industry, it is used as a sweetener, a fat substitute and as a vehicle to increase the fibre content of the diet (Roberfroid, 2007). It is also used as a livestock feed and pet food (Verdonk, Shim, Van Leeuwen, & Verstegen, 2005). It can be used for production of ultrahigh fructose syrup, bioethanol as well as chemicals like citric acid, 2,3-butanediol etc. (Chi et al., 2011). Inulin derivatives are used as green antiscalants in industrial water treatment processes (Mavredaki, Stathoulopoulou, Neofotistou, & Demadis, 2007). It has been classified as a bifidogenic prebiotic (Veereman, 2007) and owing to their anticarcinogenic properties (Korbelik & Cooper, 2007), inulin derivatives are being used as colonic drug delivery systems (Pitarresi et al., 2008).

From a chemical point of view, inulin is a polydisperse fructan. Its structural motif consists mainly, if not exclusively of β (2 → 1) fructosyl fructose units (F_m) with normally, but not necessarily, one glucopyranose unit at the reducing end (GF_n) (De Bruyn, Alvarez, Sandra, & De Leenheer, 1992). Inulin containing glucopyranose unit is not a reducing sugar. The fructose units in the polysaccharide are all present in the furanose form, except when the reducing end consists of fructose (Rogge & Stevens, 2004). When this is the case, terminal fructose is present in the pyranose form giving to inulin reducing properties. In general, reducing properties of inulin are a rarity since chain termination by glucopyranose is dominant.

1.2. Graft copolymerization: processes, mechanism and role of microwave

A graft copolymer consists of a long sequence of one monomer, referred to as the backbone polymer (main chain) with one or more branches (grafts) of a different monomer (Gowariker, Vishwanathan, & Sreedhar, 1986). Synthetic protocols for graft polymerization can be classified into three main groups, namely: a) free radical polymerization b) ionic and ring opening polymerization and c) living radical polymerization. The above polymerization techniques broadly involve following mechanistic approaches: a) 'grafting-to' b) 'grafting-from' and c) 'grafting-through', the

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polysaccharide (Odian, 2004). The 'grafting-from' approach mentioned here involves the use of a natural polymer with pendant functional group that can be activated to initiate the tethering of an incoming monomer. This is one of the most commonly used approaches and gives products with high graft density owing to easy accessibility of the reactive groups (Roy, Semsarilar, Guthrie, & Perrier, 2009).

In case of free radical polymerization, grafting process starts with generation of radical sites on the backbone polymer (polysaccharide in this case) using an external agent. Once the free radical sites are generated, the monomer (i.e., vinyl or acrylic substrate) can get anchored to the backbone polymer in the chain propagation step; resulting in formation of grafted products. All the various modes of graft copolymer synthesis, whether utilizing high energy UV radiation or Microwave, primarily differ in the ways of generation of free radicals on the backbone polymer.

Use of microwave radiations is one of the most contemporary techniques in graft copolymer synthesis. Their utility stems from the fact that they cause selective and targeted excitation of only the polar bonds, resulting in their cleavage and consequent generation of free radical sites (Sen, Kumar, Ghosh, & Pal, 2009). The 'C–C' backbone of the preformed polymer being relatively non polar, remains unaffected by the microwave radiation. Thus, the structural integrity of the backbone remains intact, leading to a superior product (Rani, Mishra, & Sen, 2013). Microwave based graft copolymer synthesis is further classified into two types: Microwave initiated synthesis (using microwave radiation alone to initiate grafting) and microwave assisted synthesis (using a synergism of microwave radiation and chemical free radical initiator to initiate grafting) (Ghosh, Sen, Jha, & Pal, 2010).

1.3. Significance of aqueous medium, coal fines flocculation and PAM chain grafting

Taking into account, environmental and safety considerations, attempts to replace toxic organic solvents by safer and more environment friendly medium present an arduous task. In this context, water appears to be a better option compared to organic solvents because of its abundance, non-toxic, non corrosive and non flammable nature. In addition, water can be contained because of its relatively higher vapour pressure as compared to other solvents, making scale up easier. Although *microwave assisted* reactions in conventional solvents have developed rapidly, the centre of attention has now shifted to greener and sustainable alternatives such as water (Dallinger & Kappe, 2007; Polshettiwar & Varma, 2008).

Coal consumption, has been for long, an important indicator of a nation's economic growth. Especially for the developing world, with its high energy requirements and abundant supply of coal, it is hard to ignore their economy's coal reliance. In this context, washing and cleaning coking coals before their varied industrial use has gained currency. The trouble though is the very process of cleaning produces effluents consisting of coal fines suspension. These coal washery effluents could pollute large stretch of water bodies but if recovered can serve as a precious fuel. Thus, we need to formulate a scheme which could not only take into account the ecological concerns but also the economic viability of the process. Flocculation aided by biodegradable polymeric flocculants seems to be a highly effective strategy in this regard (Pal, Sen, Karmakar, Mal, & Singh, 2008; Tripathy, Pandey, Karmakar, Bhagat, & Singh, 1999).

Tethering synthetic polymers onto natural polymers results in formation of adducts having controlled biodegradability and longer shelf life. PAM family of polymers and copolymers is a highly useful and multifaceted group in this regard, owing to their properties (Caulfield, Qiao, & Solomon, 2002). They have versatile tailorability and the amide groups can be tuned according to the requirement (Sen, Ghosh, Jha, & Pal, 2011; Yamamoto & Sefton, 1996). Grafting, synthetically stitches flexible PAM branches on the rigid polysaccharide backbone, resulting in better approachability to the colloidal particles and thus better flocculation efficacy (Nayak & Singh, 2001). In addition, low toxicity and low operational investments required for these water soluble, high molecular weight compounds, makes the use of PAM flocculants highly desirable.

1.4. Plan of investigation

The study described in this paper (Scheme 1) involves the synthesis of graft chains of polyacrylamide (PAM) onto the backbone of inulin (In), resulting in formation of polyacrylamide grafted inulin (In-g-PAM). The synthesis has been carried out by *aqueous microwave assisted method*, which involves a synergism of microwave radiations and ceric ammonium nitrate (CAN) to initiate the grafting reaction in aqueous medium. The flocculation efficacy of the grafted product has been studied in coal fines effluent towards its application in coal washery effluent treatment.

2. Experimental

2.1. Materials

2.1.1. Materials for synthesis

Inulin was procured from SRL, Mumbai, India and acrylamide was obtained from E. Merck, Germany. Ceric ammonium nitrate was supplied by Loba Chemie, Mumbai, India. Acetone was purchased from Rankem, New Delhi, India. All the chemicals were used as received, without further purification.

2.1.2. Materials for flocculation

The non-coking coal sample utilized in the present study was collected from Piparwar Coal mines, Central Coalfields Limited, Jharkhand, India. Proximate analysis results of the coal sample are given in Supplementary Table 1. The coal sample was pulverized to –200 mesh ASTM (i.e., size <75 μm) for conducting the experiments.

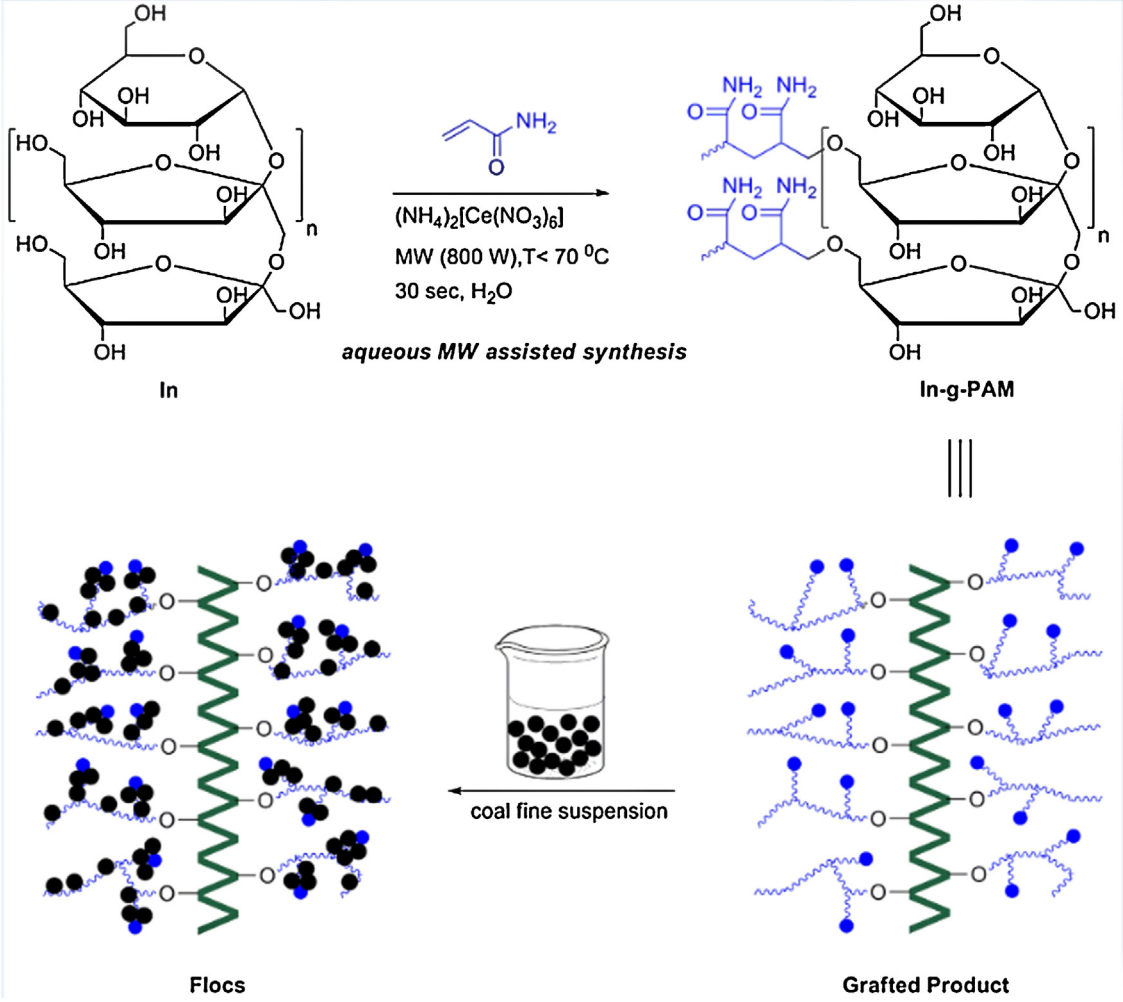
2.2. Synthesis

2.2.1. Aqueous microwave assisted synthesis of polyacrylamide grafted inulin (In-g-PAM)

1 g of inulin was dissolved in 40 mL distilled water and to it was added desired amount of acrylamide. The above solution was mixed well and transferred to the reaction vessel (250 mL borosil beaker) followed by addition of catalytic amount of free radical initiator, ceric ammonium nitrate. The reaction vessel was placed on the turntable of a microwave oven and microwave irradiation at a power of 800 W was performed. Periodically, the microwave irradiation was paused just as the reaction mixture starts boiling (~65 °C) and was cooled by placing the reaction vessel in cold water. This was done to keep any probability of competing homopolymer formation reaction to the minimum.

This *microwave irradiation–cooling* cycle was repeated until a gel like mass was left or up to 3 min of irradiation time (if no gelling took place). The reaction vessel and its contents were then cooled and kept undisturbed to complete the grafting reaction. Later, the gel like mass left in the reaction vessel was poured into excess of acetone. The resulting precipitate of graft copolymer was collected and was dried in a hot air oven. Subsequently, it was pulverized, sieved and purified. The percentage grafting of this microwave assisted synthesized In-g-PAM was evaluated as:

$$\%\text{Grafting} = \frac{\text{wt. of graft copolymer} - \text{wt. of polysaccharide}}{\text{wt. of polysaccharide}} \times 100.$$



Scheme 1. Plan of investigation.

The synthesis details of various grades of the graft copolymer have been shown in Table 1.

2.2.2. Purification of the graft copolymer

Any occluded PAM formed by competing homopolymer reaction was removed from the synthesized graft copolymer, by soxhlet extraction using acetone as a solvent for 72 h (Yang et al., 2012).

2.3. Characterization

2.3.1. Intrinsic viscosity measurement

Viscosity measurements of the aqueous polymer solutions were carried out with an Ubbelohde viscometer (capillary diameter 0.46 mm) at 25 °C. The pH of the solution was kept neutral and 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 ($\eta_{rel} = t/t_0$) was obtained. Specific viscosity (η_{sp}), relative viscosity (η_{rel}), reduced viscosity (η_{red}) and inherent viscosity (η_{inh}) were calculated using following relations:

$$\eta_{sp} = \eta_{rel} - 1$$
$$\eta_{red} = \eta_{sp}/C$$
$$\eta_{inh} = \ln \eta_{rel}/C$$

where 'C' represents polymer concentration in g/dL.

Subsequently, the reduced viscosity (η_{red}) and the inherent viscosity (η_{inh}) were plotted against concentration. The intrinsic viscosity was obtained from the point of intersection after

Table 1
Synthesis details of polyacrylamide grafted inulin (In-g-PAM) grades.

Polymer grades	Wt. of inulin (g)	Wt. of acrylamide (g)	Wt. of CAN (g)	Time of irradiation (up to gel formation) (s)	%Grafting	Intrinsic viscosity (dL/g)
Inulin						0.07
In-g-PAM 1	1	10	0.1	30	1279.4	0.86
In-g-PAM 2	1	10	0.2	30	1647.8	1.61
In-g-PAM 3	1	10	0.3	30	1514.3	1.29
In-g-PAM 4	1	05	0.2	30	0691.6	0.62
In-g-PAM 5	1	15	0.2	30	1947.5	2.56

$\%\text{Grafting} = \frac{\text{wt. of graft copolymer} - \text{wt. of polysaccharide}}{\text{wt. of polysaccharide}} \times 100.$

extrapolation of two plots (i.e. η_{red} versus C and ln η_{inh} versus C) to zero concentration (Collins, Bares, & Billmeyer, 1973). The intrinsic viscosity thus evaluated for various grades of the graft copolymer has been reported in Table 1.

2.3.2. Elemental analysis

The elemental analysis of inulin (In) and that of different grades of grafted inulin (In-g-PAM) was undertaken with an Elemental Analyzer (Model: Vario EL III, Elementar, Germany). The estimation of elements, i.e., carbon, hydrogen, nitrogen and oxygen were undertaken. The results have been summarized in Table 2.

2.3.3. FTIR spectroscopy

The FTIR spectrums of inulin, PAM and In-g-PAM 5 were recorded in solid state, by KBr pellet method using a FTIR spectrophotometer (Model: IR-Prestige 21, Shimadzu, Japan) between 400 and 4000 cm^{-1}. The concerned spectrums are shown in Fig. 1(a)–(d).

Table 2
Elemental analysis of In and In-g-PAM grades.

Polymer grade	% C	% H	% N	% O
Inulin	39.24	6.92	0.00	53.84
PAM	41.65	7.61	15.99	34.75
In-g-PAM 1	43.40	8.44	14.93	33.23
In-g-PAM 2	44.69	8.54	13.81	32.96
In-g-PAM 3	43.78	8.39	12.90	34.93
In-g-PAM 4	43.35	8.15	14.52	33.98
In-g-PAM 5	42.41	8.25	16.08	33.26

2.3.4. TGA studies

The thermogravimetric analysis (TGA) of inulin, PAM and that of In-g-PAM 5 were carried out with TGA instrument (Model: DTG-60, Shimadzu, 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 °C/min. The resulting TGA curves are shown in Fig. 2(a)–(d).

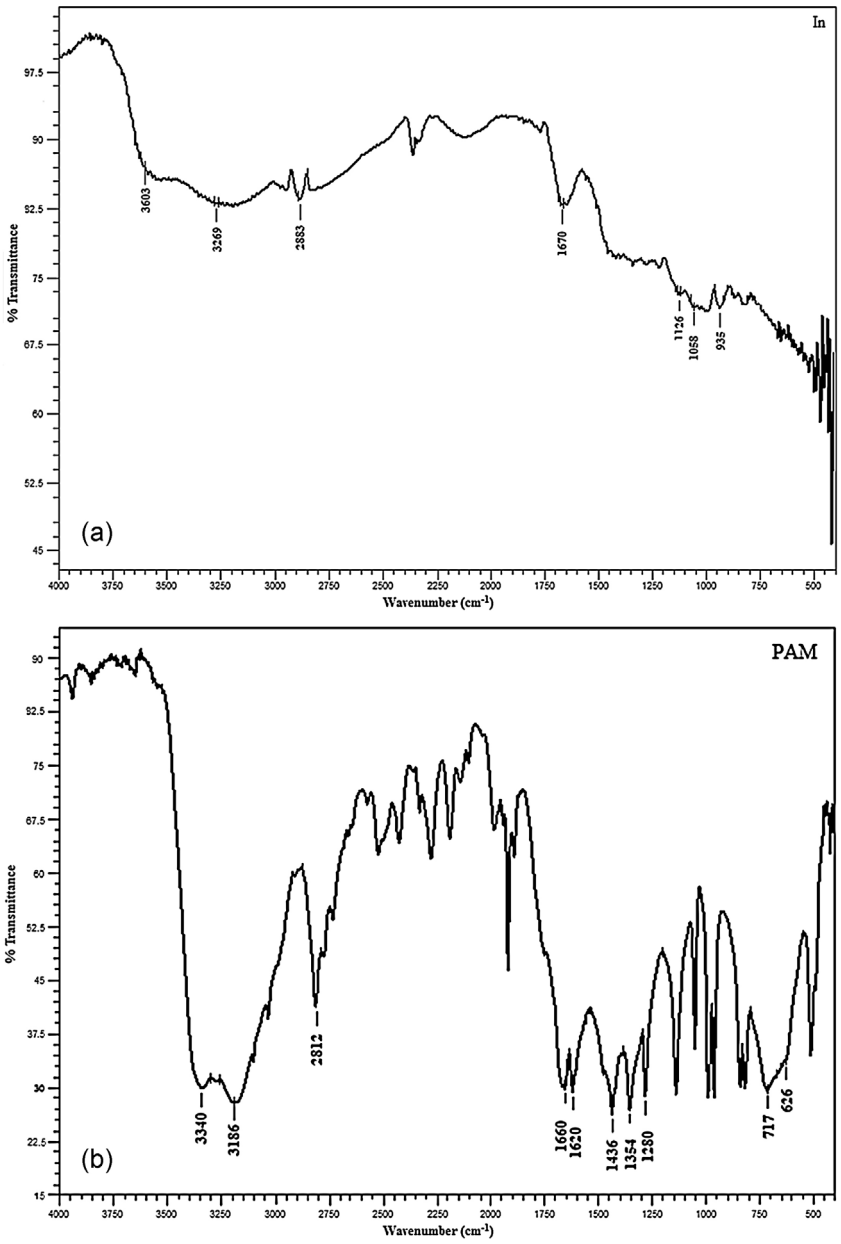


Fig. 1. FTIR spectrum of (a) In, (b) PAM, (c) In-g-PAM 5 and (d) comparative.

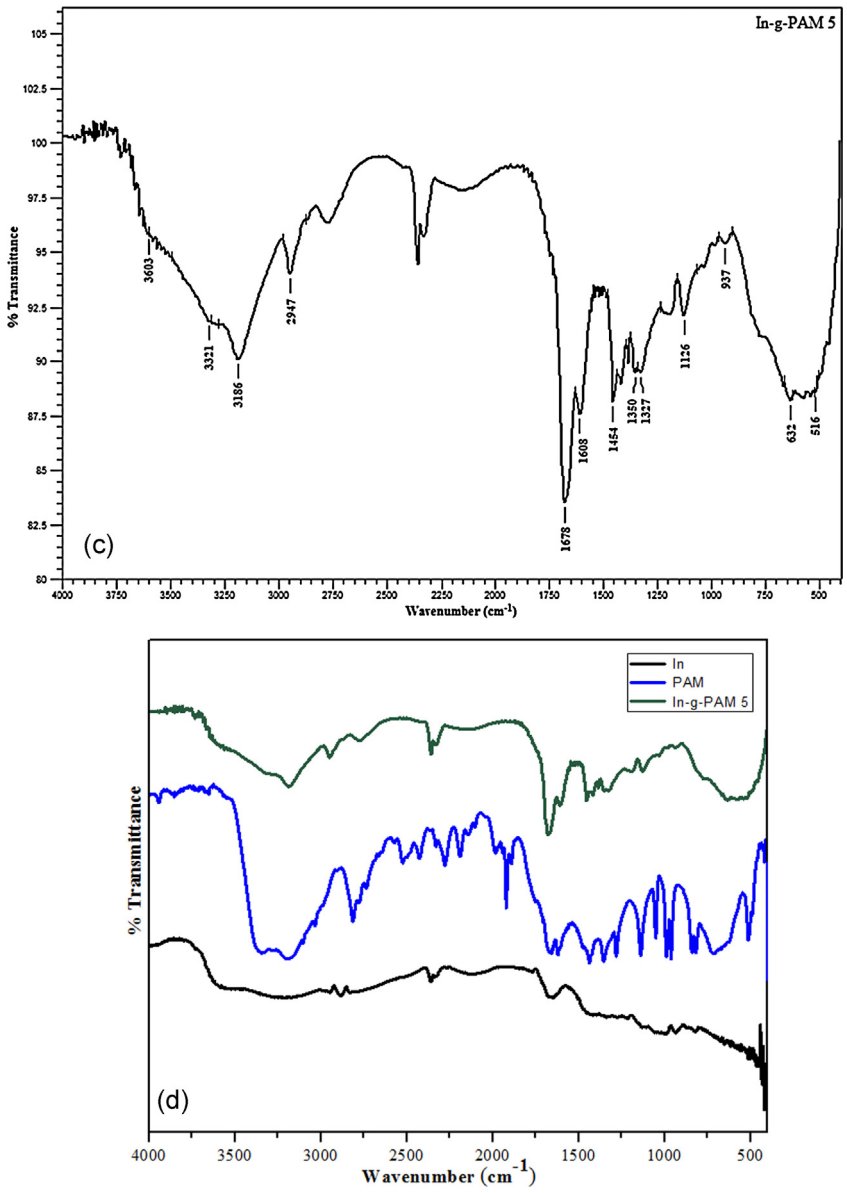


Fig. 1. (*Continued*)

2.3.5. Scanning electron microscopy

Surface morphology of inulin (Fig. 3(a) and (b)) and In-g-PAM 5 (Fig. 3(c) and (d)) were analyzed in scanning electron microscopy (SEM) in powdered form (Model: JSM-6390LV, Jeol, Japan).

2.4. Flocculation study in coal fines suspension

Flocculation tests of coal suspensions were carried out by using jar test apparatus. Flocculation efficacy of various synthesized grades of In-g-PAM and that of inulin (starting material) were studied by standard jar test procedure, in 1% coal fines suspension.

All flocculation experiments were carried out in jar test apparatus (Make: Simeco, Kolkata, India). The test protocol involved taking a measured quantity (800 mL) of the 1% coal fines suspension in one litre borosil beakers. Calculated amount of the flocculant (inulin or various grades of In-g-PAM) was added in concentrated solution form (except in case of blank, where no flocculant was added) to achieve the desired dosage (ranging from 0 ppm to 1.25 ppm). The solutions were identically stirred (in jar test apparatus), at 160 rpm for 30 s, 60 rpm for 5 min, followed by settling time of 5 min. Afterwards, supernatant liquid was collected from each jar and optical density was measured in a calibrated spectrophotometer (DR/2400, Hach®) at λ_{max} 520 nm. The flocculation efficacy thus studied for inulin and various grades of In-g-PAM have been graphically compared in Fig. 4(a).

The settling test utilized a 100 mL stoppered graduated cylinder containing 1 wt% coal fines suspension. The flocculant (In-g-PAM or inulin) was added in concentrated solution form, to affect the optimized dosage (as determined by the jar test procedure described above) and the cylinder turned upside down 10 times. After mixing, the cylinder was set upright and the height of the clear water–suspension interface measured with respect to time. The result was graphically plotted as interfacial height versus settling time, Fig. 4(b) and consequently the settling velocity was calculated in each case and correlation graph was drawn, Fig. 4(c).

3. Results and discussions

3.1. Synthesis

In-g-PAM has been synthesized by microwave assisted method using aqueous medium. Various grades of the graft copolymer were

synthesized by varying the ceric ammonium nitrate (CAN) and acrylamide (monomer) concentration. The synthetic details have been tabulated in Table 1. The optimized grade has been determined on the basis of its higher percentage grafting and intrinsic viscosity (which is proportional to molecular weight). The approach of synthesis involved optimization with respect to CAN, keeping the acrylamide concentration constant (i.e., In-g-PAM 1, In-g-PAM 2, In-g-PAM 3) followed by optimization with respect to acrylamide, keeping the CAN concentration as optimized before (i.e., In-g-PAM 2, In-g-PAM 4, In-g-PAM 5). From Table 1, it is obvious that the grafting is optimized at acrylamide concentration of 15 g and CAN concentration of 0.2 g in the reaction mixture (~50 mL), when the microwave power is maintained at 800 W.

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 (Greenwood & Earnshaw, 1997). Ce^{IV} takes electrons from C-6 alcoholic oxygen in inulin 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 polysaccharide, from where the graft chains grow. The proposed mechanism of microwave assisted grafting has been illustrated in Scheme 2.

3.2. Characterization

3.2.1. Estimation and interpretation of intrinsic viscosity

The intrinsic viscosity was evaluated for inulin and for all the synthesized grades of In-g-PAM, as shown in Table 1. The very low intrinsic viscosity of parent polysaccharide, inulin is in conformity with the earlier reported values (Dan, Ghosh, & Moulik, 2009; Giannouli, Richardson, & Morris, 2004). Intrinsic viscosity is practically the hydrodynamic volume of the macromolecule in the solvent (water in this case). As clear from Table 1, intrinsic viscosities of all the grades of In-g-PAM are greater than that of inulin. This is due to the increase in hydrodynamic volume resulting from the grafting of the PAM chains on the main polymer backbone (inulin). These tethered PAM chains increase hydrodynamic volume either by their own contribution or by uncoiling of the polysaccharide chains through steric hindrance to intra molecular bonding.

Further, the increase in intrinsic viscosity of synthesized grades is in good agreement with Mark–Houwink–Sakurada relationship (intrinsic viscosity $\eta = KM^{\alpha}$, where K and α are constants, both related to stiffness of the polymer chains). In accordance with the above relation, increase in intrinsic viscosity is due to increase in molecular weight (M) as a result of the grafted PAM chains.

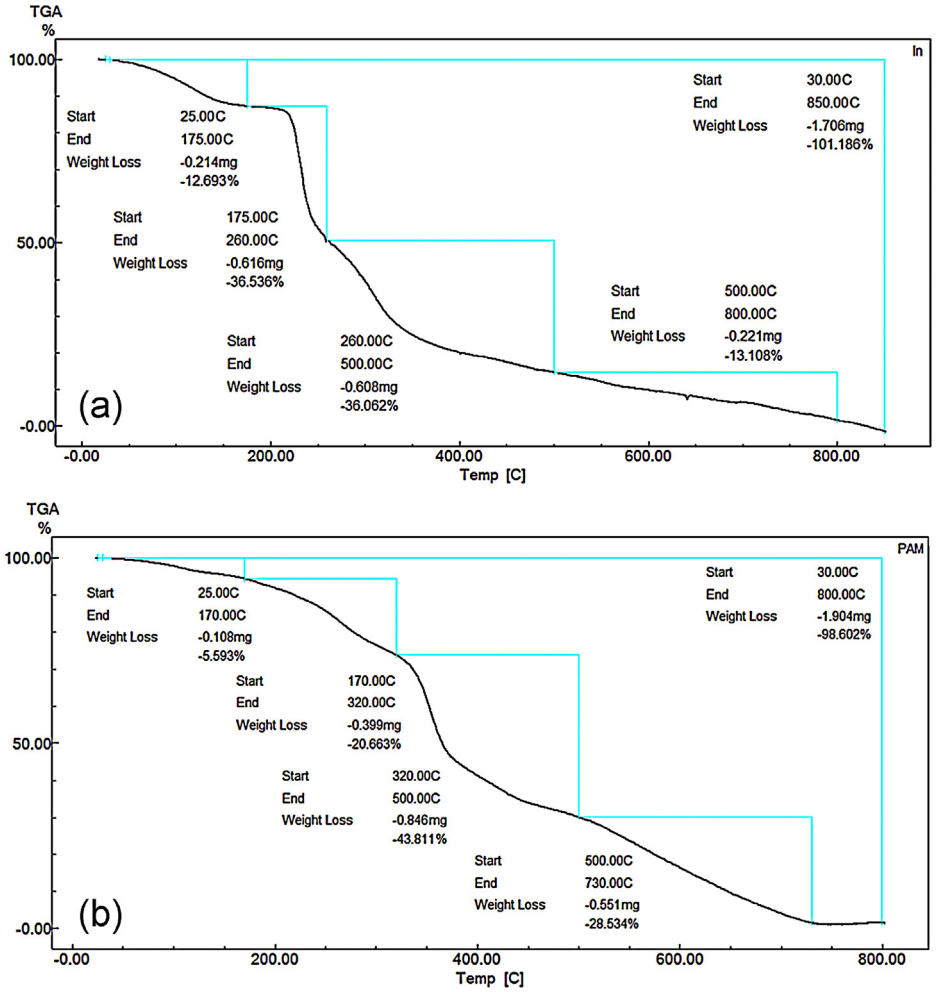


Fig. 2. TGA of (a) In, (b) PAM, (c) In-g-PAM 5 and (d) comparative.

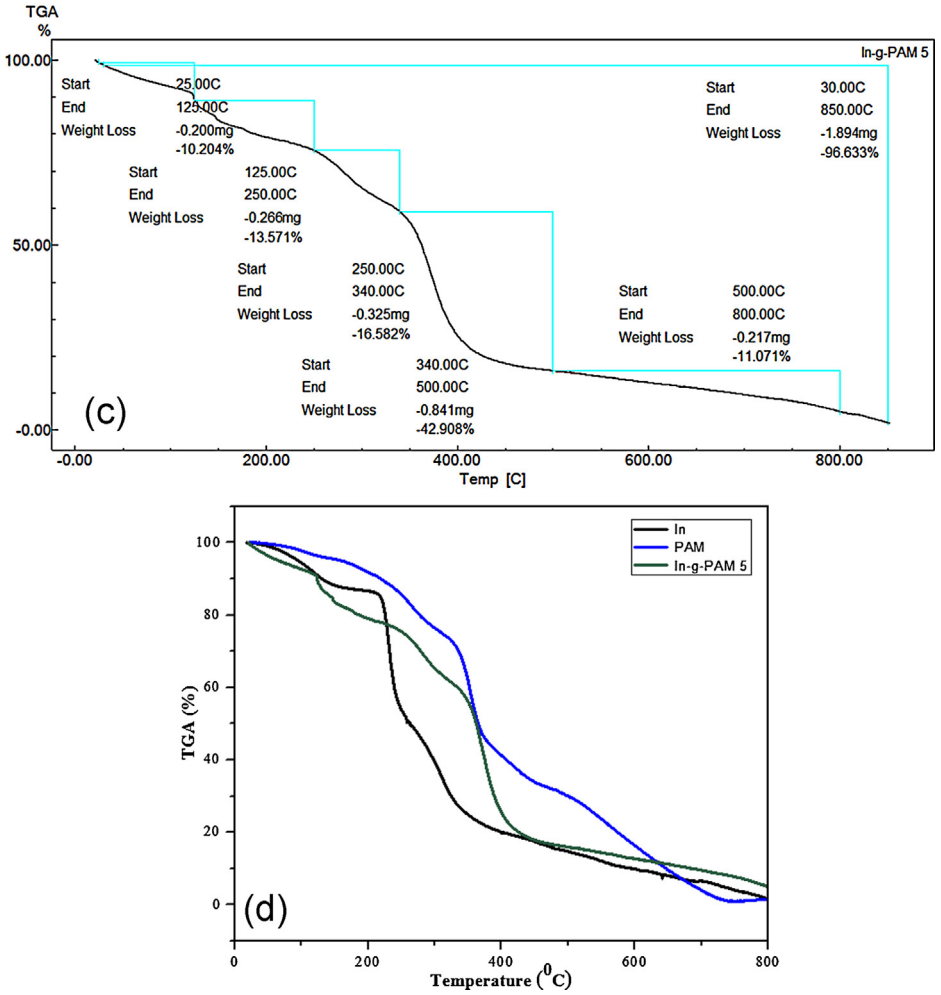


Fig. 2. (*Continued*)

3.2.2. Elemental analysis

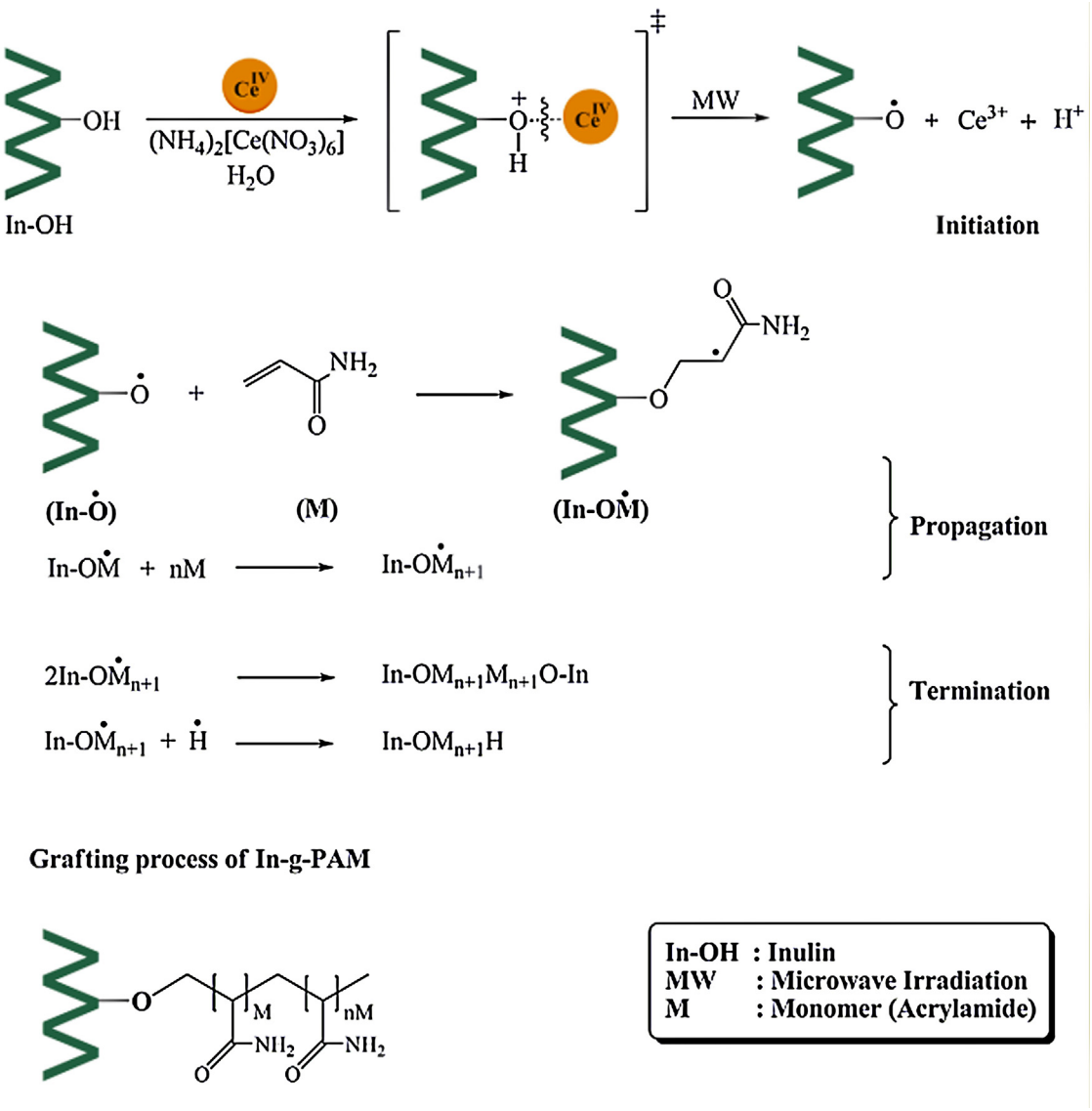
The results of elemental analysis for inulin (In), polyacrylamide (PAM) and that of various grades of polyacrylamide grafted inulin (In-g-PAM) are given in Table 2. The data clearly shows that there is a considerable percentage of nitrogen in the graft copolymers, which can be attributed to the presence of grafted PAM chains. Of all the grafted adducts, nitrogen content is significant in In-g-PAM 5 indicating increased PAM content in the reaction feed as well as the graft copolymer.

3.2.3. FTIR spectroscopy

As evident from Fig. 1(a), inulin has a broad O—H stretching peak centred at 3269 cm^{-1}, C—H stretching peak at 2883 cm^{-1} and C—O—C stretching peak at 1058 and 935 cm^{-1} respectively. In case of PAM (Fig. 1 (b)), a broad double humped peak at 3342 and 3196 cm^{-1} is for the N—H asymmetric and N—H symmetric stretch of the NH_2 group. Two bands at 1654 and 1620 cm^{-1} are attributed to the C=O stretch and N—H bending. The peak at 2812 cm^{-1} is due to C—H stretch and 1436 cm^{-1} peak corresponds to CH_2 scissoring vibration. Other peaks at 1354 and 1280 cm^{-1} are due to C—N stretch and CH_2 twist. A broad N—H out of plane bend appears in ~600–750 cm^{-1} region. From Fig. 1(c) of In-g-PAM 5, it is clear that all the peaks of inulin and PAM are present in the grafted product. O—H stretching band of inulin and N—H stretching band of amide group of PAM overlap with each other leading to a broad band in the region ~3100–3600 cm^{-1}. Other peaks at 1678, 1608 and 1350 cm^{-1} can be attributed to vibrations of C=O stretch, N—H bend and C—N stretch of the grafted PAM chains. Peaks at 1454 and 1327 cm^{-1} correspond to CH_2 scissoring and CH_2 twisting and those at 1126 and 937 cm^{-1} are attributed to C—O—C stretch. Out of plane N—H wagging is responsible for a broad band of medium intensity in the ~500–650 cm^{-1} region. The comparative IR spectra of In, PAM and In-g-PAM 5 (Fig. 1(d)), gives a clear visualization of the change in group frequencies that has occurred as a result of grafting.

3.2.4. Thermogravimetric analysis (TGA)

The TGA curves of inulin, PAM and In-g-PAM 5 are shown in Fig. 2(a)–(c). In case of inulin, four distinct zones are observed where the weight is being lost. The initial weight loss (25–175 °C) is due to the presence of small amount of moisture in the sample. The second zone (175–260 °C) is as a result of decomposition of biopolymer and the third zone (260–500 °C) is due to combustion of inulin. Fourth zone (500–800 °C) corresponds to complete degradation of inulin. Major weight loss (~73%) in thermograph of inulin can be attributed to second and third regions (175–500 °C). The TGA curve of PAM shows four distinct zones. The first zone (25–170 °C) is due to weight loss from release of both surface and matrix-bound water from the polymer. The second zone (170–320 °C) can be attributed to inter-and intramolecular imidization reactions and subsequent release of H_2O, NH_3, CO_2 as by-products. Third zone (320–500 °C) is characterized by the decomposition of imides to form nitriles and release of volatiles such as CO_2 and H_2O. Fourth zone (500–730 °C) is predominately due to random bond scission of the polymeric



Scheme 2. Proposed mechanism for aqueous microwave assisted synthesis of In-g-PAM.

main chain backbone forming long chain hydrocarbons. In the case of In-g-PAM 5, first region (25–125 °C) is due to loss of moisture. The second and third zone in the (125–340 °C) range corresponds to degradation and combustion of main backbone of inulin. Fourth zone (340–500 °C) is due to degradation of grafted PAM chains and the fifth zone (500–800 °C) refers to complete degradation of polymer. From the comparative TGA curves of In, PAM and In-g-PAM 5 (Fig. 2(d)), it is clear that the grafted product is more stable as compared to starting polysaccharide, inulin. This further confirms the enhanced thermal stability of parent polysaccharide due to grafted PAM chains.

3.2.5. Scanning electron microscopy (SEM) analysis

SEM micrographs of In and In-g-PAM 5 are shown in Fig. 3(a)–(d). Inulin micrographs consist of somewhat spherical to elongated entities with an overall granular morphology. Grafting of PAM chains have resulted in a clear and distinct change in surface morphology with granular pattern giving way to a porous structure.

3.3. Flocculation characteristics in coal fines suspension

The flocculation study in 1% coal fines suspension in jar test apparatus, for dosage varying between 0.25 ppm and 1.25 ppm has been shown in Fig. 4(a). All the grades of grafted inulin have shown better flocculation efficacy than the starting material. This is due to their higher hydrodynamic volume (i.e., intrinsic viscosity) as evidenced in Table 1. The higher hydrodynamic volume of the macromolecule leads to higher flocculation efficacy (Brostow, Pal, & Singh, 2007). There is a direct correlation evidenced for all grades of In-g-PAM. Higher the percentage grafting, higher is the intrinsic viscosity. Higher the intrinsic viscosity, higher is the flocculation efficacy.

Evidently, among the various grafted grades, the best grade (In-g-PAM 5) showed maximum flocculation efficacy due to its highest hydrodynamic volume (i.e., intrinsic viscosity). The much higher flocculation efficacy of the grafted product than the original polysaccharide confirms Singh's easy approachability model (Singh et al., 2000).

Coal is a heterogeneous solid and its surface contains both hydrophilic as well as hydrophobic sites of varying degrees. The

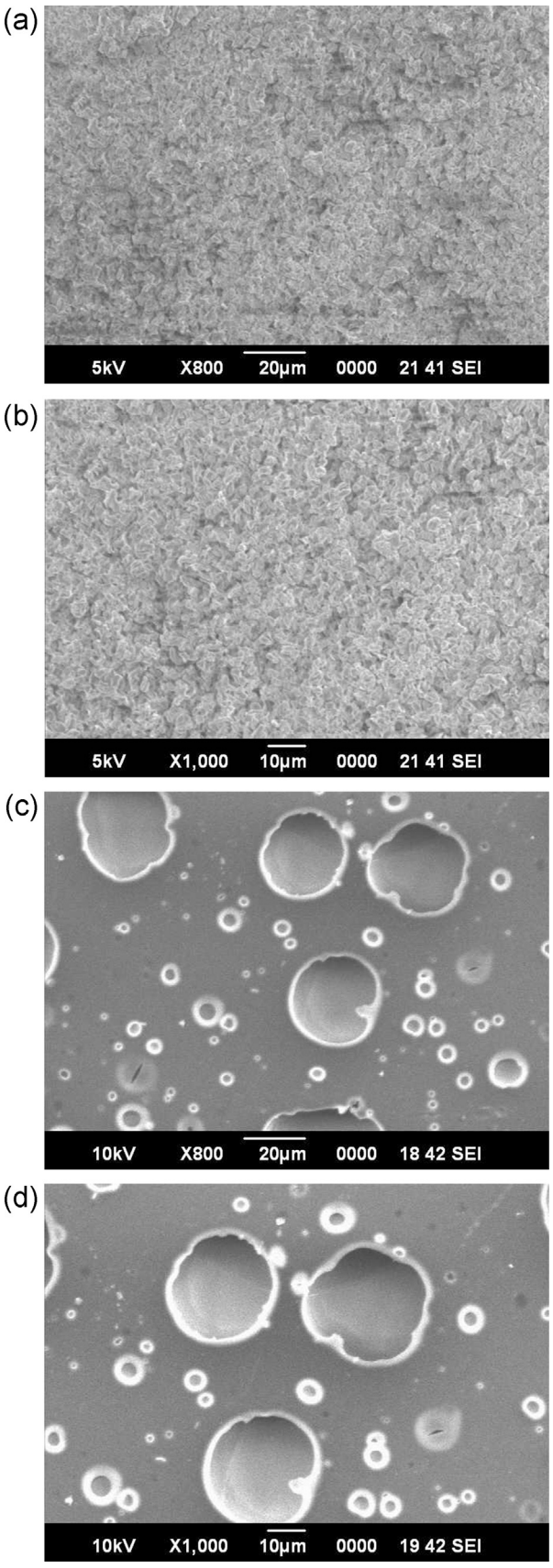


Fig. 3. SEM morphology of (a) In (800× magnification), (b) In (1000× magnification), (c) In-g-PAM 5 (800× magnification) and (d) In-g-PAM 5 (1000× magnification).

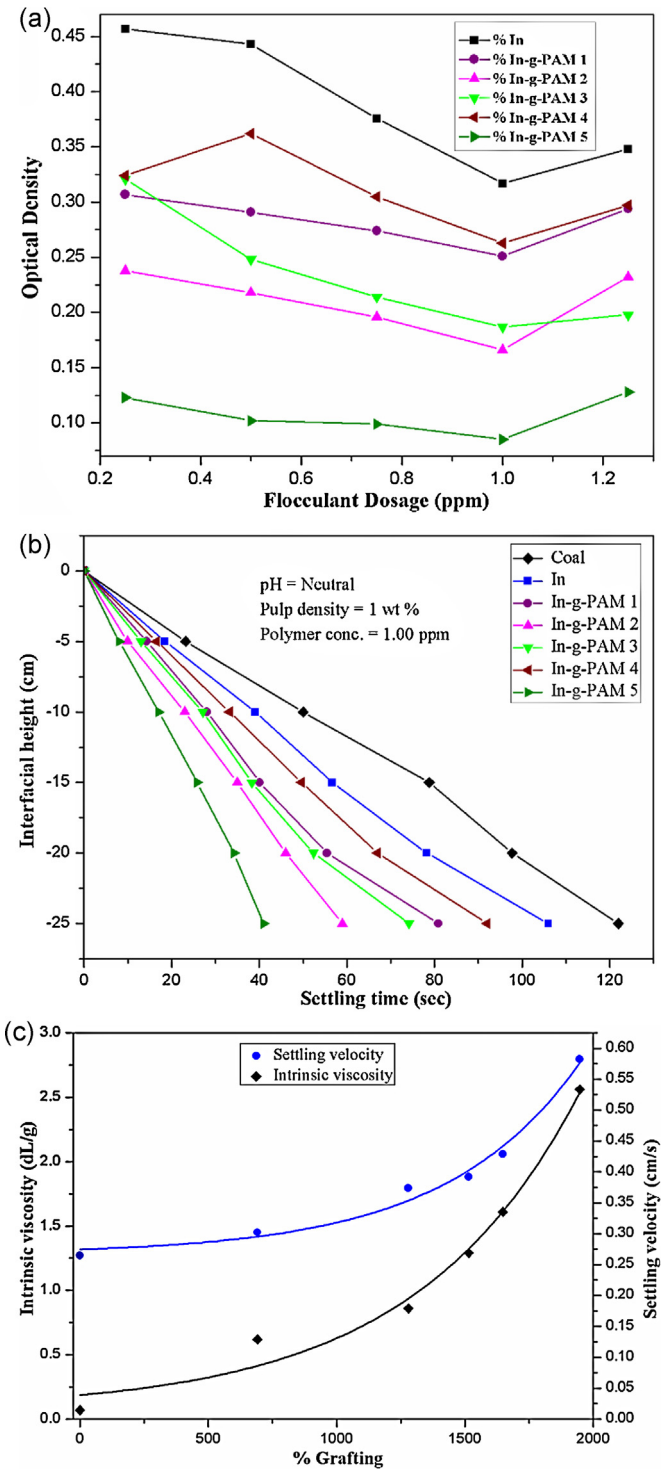


Fig. 4. Flocculation profile in 1% coal fines suspension of In and In-g-PAM grades (a) jar test, (b) settling test and (c) settling velocity and intrinsic viscosity as a function of % grafting.

hydrophilic region consists of inorganic or polar organic surface groups (oxygenated surface functionalities particularly carboxyl, carbonyl and alcoholic groups) whereas the hydrophobic surface regions are primarily non-polar organic moieties (Abotsi, Bota, Saha, & Mayes, 1996). This distribution of chemical moieties on coal surface is of direct significance in interfacial processes and a fundamental knowledge of their distribution is essential to design efficient flocculation systems. Adsorption of non-ionic,

grafted derivatives on coal surface is predominately by H-bonding as the polymer is not expected to have any residual charge (Somasundaran, Mehta, Yu, & Krishnakumar, 2008). This is followed by formation of aggregates wherein one segment of the adsorbed polymer forms a bridge with tail of another adsorbed polymer on the neighbouring particle.

For all the polymers studied, there is an optimal dosage at which the flocculation efficacy is maximum beyond which the flocculation decreases. This behaviour of the flocculation curve confirms the *bridging mechanism* (Ruehrwein & Ward, 1952). The optimal dosage of In-g-PAM 5 as flocculant, in 1% coal fines suspension is at 1.00 ppm. This small dosage of grafted product indicates the miniscule amount of the chemical sufficient to effect flocculation.

Settling tests were carried out in 1 wt% coal fines suspension and the settling characteristics of inulin and its various grafted grades are illustrated in Fig. 4(b). From the settling curves above, it is observed that 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. Settling velocity is calculated from the slope of the linear portion of the settling curves and has been given in Supplementary Table 2. In the present study, the natural settling velocity of coal suspension is 0.190 cm/s while that of In-g-PAM 5 is 0.582 cm/s. In conformity with the jar test results discussed above, In-g-PAM 5, with the highest percentage grafting has the highest settling velocity. This relationship of higher the percentage grafting, higher the settling rate is followed by the remaining grafted grades as well. The greater the settling velocity of the floc containing contaminants, the greater is its flocculation performance, as illustrated by In-g-PAM 5. The graph showing correlation between settling velocity, percentage grafting and intrinsic viscosity has been plotted in Fig. 4(c).

4. Conclusion

Polyacrylamide grafted inulin (In-g-PAM) has been synthesized by *aqueous microwave assisted* technique. The synthesized grades of this graft copolymer were characterized through various physicochemical techniques. The flocculation efficacy of the graft copolymer was studied through standard jar test and settling test procedure in coal fines suspension and was compared to that of the parent polysaccharide, inulin at a dosage ranging from 0.25 ppm to 1.25 ppm. In-g-PAM grade 5 with highest hydrodynamic volume (i.e., intrinsic viscosity) and highest sedimentation velocity showed the maximum flocculation efficacy, as predicted by *'Brostow, Pal and Singh model of flocculation*'. The higher flocculation efficacy of the grafted product than the original polysaccharide also confirms the *'Singh's easy approachability model*' to grafted PAM systems. The high flocculation efficacy of In-g-PAM 5 (optimized dosage of 1.00 ppm) in coal fines suspension makes it a superior flocculant than the starting material for the treatment of coal washery effluents.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2013.07.082.

References

Abotsi, G. M. K., Bota, K. B., Saha, G., & Mayes, S. (1996). Effects of surface active agents on molybdenum adsorption onto coal for liquefaction. *Prep. Pap.-American Chemical Society, Division of Fuel Chemistry*, *41*, 984–987.

Brostow, W., Pal, S., & Singh, R. P. (2007). A model of flocculation. *Materials Letters*, *61*, 4381–4384.

Caulfield, M. J., Qiao, G. G., & Solomon, D. H. (2002). Some aspects of the properties and degradation of polyacrylamides. *Chemical Reviews*, *102*, 3067–3083.

Chi, Z.-M., Zhang, T., Cao, T.-S., Liu, X.-Y., Cui, W., & Zhao, C.-H. (2011). Biotechnological potential of inulin for bioprocesses. *Bioresource Technology*, *102*, 4295–4303.

Collins, E. A., Bares, J., & Billmeyer, F. W. (1973). *Experiments in polymer science*. New York: John Wiley & Sons.

Dallinger, D., & Kappe, C. O. (2007). Microwave-assisted synthesis in water as solvent. *Chemical Reviews*, *107*, 2563–2591.

Dan, A., Ghosh, S., & Moulik, S. P. (2009). Physicochemical studies on biopolymer inulin: A critical evaluation of its self-aggregation, aggregate-morphology, interaction with water and thermal stability. *Biopolymers*, *91*, 687–699.

De Bruyn, A., Alvarez, A. P., Sandra, P., & De Leenheer, L. (1992). Isolation and identification of β-D-fructofuranosyl-(2,1)-D-fructose, a product of the enzymatic hydrolysis of the inulin from *Cichorium intybus*. *Carbohydrate Research*, *235*, 303–308.

Ghosh, S., Sen, G., Jha, U., & Pal, S. (2010). Novel biodegradable polymeric flocculant based on polyacrylamide-grafted tamarind kernel polysaccharide. *Bioresource Technology*, *101*, 9638–9644.

Giannouli, P., Richardson, R. K., & Morris, E. R. (2004). Effect of polymeric cosolutes on calcium pectinate gelation. Part 2. Dextrans and inulin. *Carbohydrate Polymers*, *55*, 357–365.

Gowariker, V. R., Vishwanathan, N. V., & Sreedhar, J. (1986). *Polymer Science*. New Age International (p) Ltd (Chapter 12)

Greenwood, N. N., & Earnshaw, A. (1997). *Chemistry of the elements* (2nd ed.). Oxford: Butterworth-Heinemann.

Kaur, N., & Gupta, A. K. (2002). Applications of inulin and oligofructose in health and nutrition. *Journal of Biosciences*, *27*, 703–714.

Korbelik, M., & Cooper, P. D. (2007). Potentiation of photodynamic therapy of cancer by complement: The effect of gamma-inulin. *British Journal of Cancer*, *96*, 67–72.

Mavredaki, E., Stathoulopoulou, A., Neofotistou, E., & Demadis, K. D. (2007). Environmentally benign chemical additives in the treatment and chemical cleaning of process water systems: Implications for green chemical technology. *Desalination*, *210*, 257–265.

Nayak, B. R., & Singh, R. P. (2001). Synthesis and characterization of grafted hydroxypropyl guar gum by ceric ion induced initiation. *European Polymer Journal*, *37*, 1655–1666.

Odian, G. (2004). *Principles of polymerization* (4th ed.). New York: John Wiley & Sons.

Pal, S., Sen, G., Karmakar, N. C., Mal, D., & Singh, R. P. (2008). High performance flocculating agents based on cationic polysaccharides in relation to coal fine suspension. *Carbohydrate Polymers*, *74*, 590–596.

Pitarresi, G., Tripodo, G., Calabrese, R., Craparo, E. F., Licciardi, M., & Giammona, G. (2008). Hydrogels for potential colon drug release by thiol-ene conjugate addition of a new inulin derivative. *Macromolecular Bioscience*, *8*, 891–902.

Polshettiwar, V., & Varma, R. S. (2008). Aqueous microwave chemistry: A clean and green synthetic tool for rapid drug discovery. *Chemistry Society Reviews*, *37*, 1546–1557.

Rani, P., Mishra, S., & Sen, G. (2013). Microwave assisted synthesis of polymethylmethacrylate grafted sodium alginate: Its application as flocculant. *Carbohydrate Polymers*, *91*, 686–692.

Roberfroid, M. B. (2007). Inulin-type fructans: Functional food ingredients. *Journal of Nutrition*, *137*, 2493S–2502S.

Rogge, T. M., & Stevens, C. V. (2004). Facilitated synthesis of inulin esters by transesterification. *Biomacromolecules*, *5*, 1799–1803.

Roy, D., Semsarilar, M., Guthrie, J. T., & Perrier, S. (2009). Cellulose modification by polymer grafting: A review. *Chemical Society Reviews*, *38*, 2046–2064.

Ruehrwein, R. A., & Ward, D. W. (1952). Mechanism of clay aggregation by polyelectrolytes. *Soil Science*, *73*, 485–492.

Sen, G., Ghosh, S., Jha, U., & Pal, S. (2011). Hydrolyzed polyacrylamide grafted carboxymethylstarch (Hyd. CMS-g-PAM): An efficient flocculant for the treatment of textile industry wastewater. *Chemical Engineering Journal*, *171*, 495–501.

Sen, G., Kumar, R., Ghosh, G., & Pal, S. (2009). Novel polymeric flocculant based on polyacrylamide grafted carboxymethylstarch. *Carbohydrate Polymers*, *77*, 822–831.

Singh, R. P., Karmakar, G. P., Rath, S. K., Karmakar, N. C., Pandey, S. R., Tripathy, T., et al. (2000). Biodegradable drag reducing agents and flocculants based on polysaccharides: Materials and applications. *Polymer Engineering & Science*, *40*, 46–60.

Somasundaran, P., Mehta, S. C., Yu, X., & Krishnakumar, S. (2008). Colloid systems and interfaces stability of dispersions through polymer and surfactant adsorption. In *Handbook of surface and colloid chemistry*. CRC Press.

Tripathy, T., Pandey, S. R., Karmakar, N. C., Bhagat, R. P., & Singh, R. P. (1999). Novel flocculating agent based on sodium alginate and acrylamide. *European Polymer Journal*, *35*, 2057–2072.

Van Loo, J., Coussement, P., De Leenheer, L., Hoebregs, H., & Smits, G. (1995). On the presence of inulin and oligofructose as natural ingredients in western diet. *Critical Reviews in Food Science and Nutrition*, *35*, 525–552.

Veereman, G. (2007). Pediatric application of inulin and oligofructose. *Journal of Nutrition*, *137*, 2585S–2589S.

Verdonk, J. M. A. J., Shim, S. B., Van Leeuwen, P., & Verstegen, M. W. A. (2005). Application of inulin-type fructans in animal feed and pet food. *British Journal of Nutrition*, *93*(Suppl. 1), S125–S138.

Yamamoto, Y., & Sefton, M. V. (1996). Hofmann degradation of acrylamide copolymer: Synthesis of amine functionalized thermoplastic hydrogel. *Journal of Applied Polymer Science*, *61*, 351–358.

Yang, Z., Yuan, B., Huang, X., Zhou, J., Cai, J., Yang, H., et al. (2012). Evaluation of the flocculation performance of carboxymethyl chitosan-g-polyacrylamide, a novel amphoteric chemically bonded composite flocculant. *Water Research*, *46*, 107–114.