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High performance polymeric flocculants based on modified polysaccharides—Microwave assisted synthesis

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ABSTRACT

New generation of polymeric flocculants has been developed by optimally grafting polyacrylamide branches on purified polysaccharide backbone in authors' laboratory. These flocculants are synergistically efficient at low doses, controlled biodegradable, shear resistant, and ecofriendly. Recently it has been observed in the authors' laboratory that graft copolymers synthesized by microwave initiated and microwave assisted methods provide a better quality of graft copolymer with higher percentage of grafting in comparison with conventional redox grafting method. The synthesized graft copolymers were characterized by variety of material characterization techniques. The microwave assisted synthesized graft copolymers show superior flocculation characteristics when compared with graft copolymers synthesized by conventional and microwave initiated method as well as with commercially available flocculant. The details of material synthesis, mechanism, characterization and applications of these novel materials in the field of flocculation have been reported.

1. Introduction

The mineral and paper processing industries require very large volume of fresh water every day. Since fresh water has become a valuable commodity, recycling and reuse of wastewater becomes indispensable for all the processing industries to reduce the processing cost and also to abide by the environmental rules and regulations (Bolto & Gregory, 2007).

The wastewater emanated from these industries contains very fine suspended particles having size in the range of 0.001–10 μm. Due to very small size and presence of surface charge, it is very difficult to bring these particles closer to make heavier mass for settling (Bratby, 2006). Sometimes these particles remain suspended for years (Ali, Pal, & Singh, 2010). Hence, removal of these colloidal particles from the wastewater becomes a serious challenge for the industries (Divakaran & Pillai, 2001; Naseer & James, 2006). Various traditional and advanced technologies have been utilized for the removal of these colloidal particles from water, such as ion-exchange, precipitation, flotation, solvent extraction, adsorption, flocculation and electrolytic methods. Among these techniques, flocculation is generally preferred for the removal of colloidal particles as well as heavy-metal ions because of its high efficiency, easy handling, and availability of various kinds of flocculants (Naseer & James, 2006). So the search for cost-effective flocculants and economic method of removing toxic heavy metal ions as well as suspended particles has also become the focus of many studies (Pal, Ghosh, Sen, Jha, & Singh, 2009; Runkana, Somasundaran, & Kapur, 2006).

Most of the suspended particles carry charge in neutral aqueous medium. To destabilize the system, inorganic coagulants such as alum, polyaluminium chloride, ferric chloride, ferrous sulfate, magnesium chloride have been used for decades (Duk et al., 2007). However, this process is strongly pH dependent and decreases the alkalinity of the water (Duk et al., 2007). Moreover, the inorganic coagulants are required in large amount to achieve effective settling rate. As a consequence, a large volume of metal hydroxide sludge is produced. This again creates disposal problem. Apart from this disposal problem, the uses of inorganic salts such as alum, polyaluminium chloride are now very much controversial due to the possible impact of residual aluminium in the recycled water on Alzheimer disease (Ali et al., 2010).

To minimize the drawbacks of inorganic coagulants, synthetic flocculants are used as alternatives due to their rapid settling and small sludge production. The flocculants bridge the approaching particles by the polymer chains (Healy & La Mer, 1964). The bridging performance of the flocculants depends on the physiochemical properties of the polymers such as, molecular weight, size and shape, charge density, hydrophobicity, adsorption density

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and conformation of the adsorbed polymer (Besra, Sengupta, & Roy, 2006).

Water soluble synthetic flocculants, mainly polyacrylamide based flocculants, with various molecular weights and charge density received great extent of utility in the industries due to their economical advantage and easy tailorability (Singh, Karmakar et al., 2000; Singh, Tripathy et al., 2000). However, these synthetic polymers are not biodegradable and their degraded products are considered hazardous because of the release of monomers that could enter in the food chain and may cause carcinogenic effect (Sharma, Dhuldhoya, & Marchant, 2006; Singh, Karmakar et al., 2000; Singh, Tripathy et al., 2000). In this respect, scientists around the world are trying to develop biopolymer based flocculants that have the potential to substitute the synthetic flocculants (Chen, Chen, & Wu, 2003).

Chemical grafting is one of the most effective methods for modifying structure and properties of biopolymers. Graft copolymerization of natural polysaccharides is becoming an important resource for developing advanced materials as it can improve the functional properties of natural polysaccharides (da Silva, de Paula, & Feitosa, 2007; Geresh et al., 2004; Singh, Tiwari, Tripathy, & Sanghi, 2006; Singh, Tripathy, Tiwari, & Sanghi, 2006). The grafted polymers are usually synthesized by conventional redox grafting method (Ali & Singh, 2009; Nayak & Singh, 2001; Rath & Singh, 2000; Singh, Pal, Krishnamoorthy, Adhikary, & Ali, 2009), by microwave irradiation (Sen, Kumar, Ghosh, & Pal, 2009; Singh, Tiwari et al., 2006; Singh, Tripathy et al., 2006), by γ-ray irradiation (Wang, Chen, Zhang, & Yu, 2008) and by using electron beam (Vahdat, Bahrami, Ansari, & Ziaie, 2007). Among these methods, microwave irradiation exhibits the most potential to synthesize the grafted polymers. This is because in microwave irradiation based synthesis, the percentage grafting depends on monomer concentration, power and exposure time of the irradiation; these factors are electronically controlled. Moreover, microwave irradiation as efficient thermal energy constitutes a very original method of heating materials, different from the classical ones. Main advantage is that, it results in almost instantaneous homogeneous heating of materials in a selective manner.

In this article, the synthesis of graft copolymers based on various polysaccharides (carboxymethylstarch, tamarind kernel polysaccharide, sodium alginate) and polyacrylamide using three methods namely conventional method, microwave initiated method and microwave assisted method, their physicochemical characterizations have been addressed. Moreover, the applicability of these synthesized biopolymers as efficient flocculants for the treatment of wastewater has also been demonstrated.

2. Experimental

2.1. Materials

Tamarind kernel polysaccharide and sodium alginate were gift samples from Hindustan Gum & Chemicals Ltd., Bhiwani, Haryana, India. Carboxymethylstarch has been synthesized in laboratory (Sen & Pal, 2009). Acrylamide was procured from E. Merck, Germany. Ceric ammonium nitrate was purchased from Loba Chemie, Mumbai, India. Analar grade of acetone and hydroquinone were supplied by S.D. Fine Chemicals, Mumbai, India. All chemicals were used as received without further purification.

Kaolin (suspension zeta potential = −4.9 mV at pH = 7) was supplied by Jyoti Chemicals, Howrah, India. The municipal sewage wastewater (suspension zeta potential = −0.34 mV at pH = 7) was collected from the main sewage system of Birla Institute of Technology, Mesra, Ranchi community.

One commercial flocculant namely Rishfloc 226 LV (Nonionic in nature; Manufacturer – Rishabh Metals and Chemicals Pvt. Ltd., Mumbai, India) was used for comparison of flocculation efficiency.

2.2. Synthesis

2.2.1. Synthesis of the graft copolymer by conventional, microwave initiated and microwave assisted methods

Grafting reaction was carried out by three different methods. The details of synthesis procedure for various methods have been depicted in Scheme 1. Conventional grafting method was carried out in a three necked round bottom flask, where as microwave based grafting was carried out using a domestic microwave oven (‘25 Litres’ LG Microwave oven Model: MG-577B). The synthesis parameters are summarized in Table 1.

2.2.2. Purification of the graft copolymer by solvent extraction method

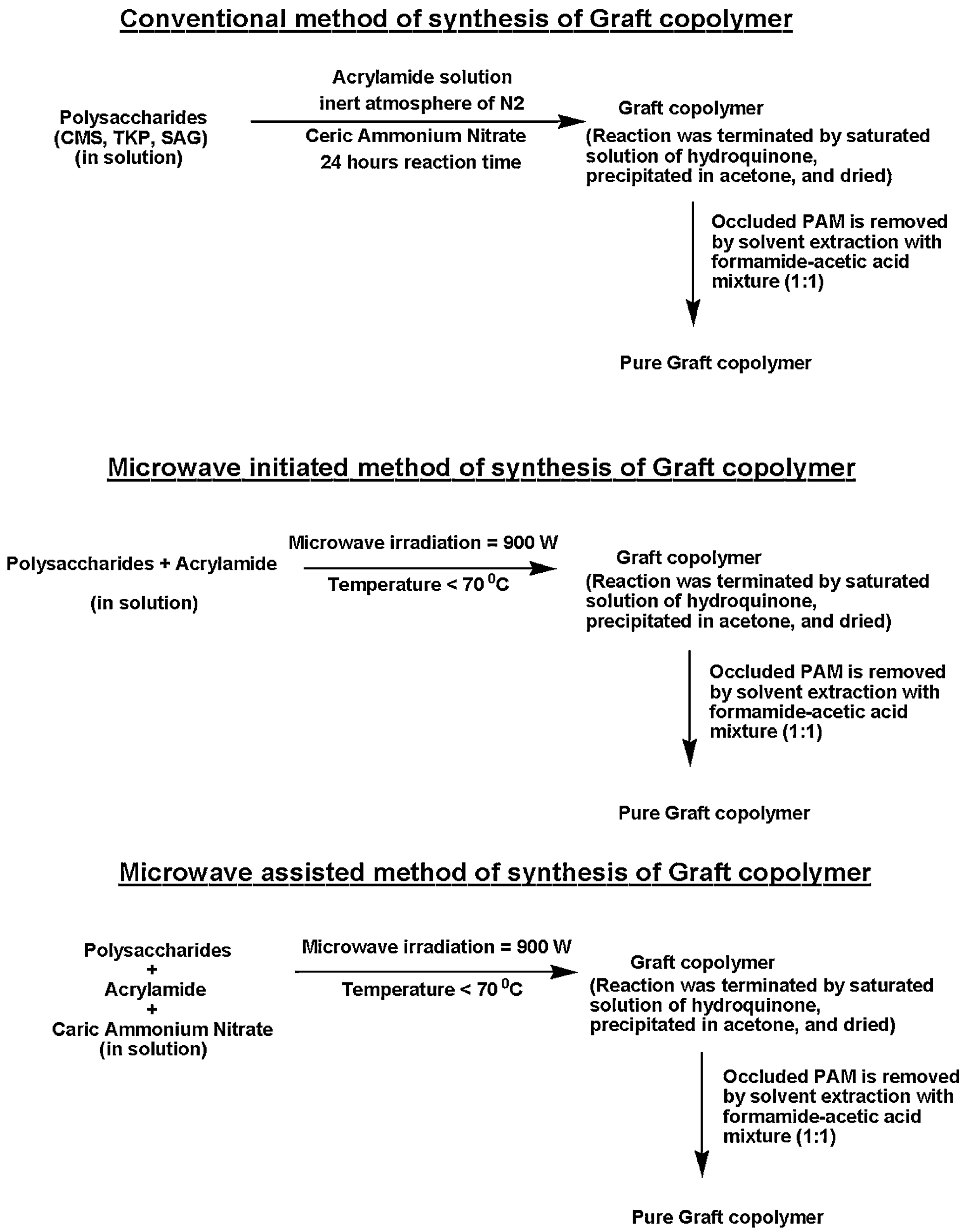
Occluded polyacrylamide (PAM) formed by competing homopolymer formation was removed from the grafted polymers by solvent extraction using a mixture of formamide and acetic acid (1:1 by volume).

Table 1
Synthesis details.

Polymer	Amount of AM (mole)	Amount of CAN (mole × 10^{-4})	% Grafting	Intrinsic viscosity (dL/g)	Mol. wt. (g/mole)	Radius of gyration (R_z)
Synthetic details of optimized grades of conventional synthesis (amount of polysaccharide = 0.0061 in each synthesis)						
TKP-g-PAM (C)	0.21	0.525	45	4.7	3.35×10^6	86.5
CMS-g-PAM (C)	0.21	0.42	47	6.8	4.30×10^6	82.0
SAG-g-PAM (C)	0.21	0.525	31	9.2	3.92×10^4	79.8

Polymer	Amount of AM (mole)	Time (min)	% Grafting	Intrinsic viscosity (dL/g)	Mol. wt. (g/mole)	Radius of gyration (R_z)
Synthetic details of optimized grades of microwave initiated synthesis (amount of polysaccharide = 0.0061 in each synthesis)						
TKP-g-PAM (MI)	0.21	3	53	5.6	5.12×10^6	91.6
CMS-g-PAM (MI)	0.14	3	50	7.4	4.79×10^6	86.6
SAG-g-PAM (MI)	0.21	3	37	11.6	4.30×10^4	84.5

Polymer	Amount of AM (mole)	Amount of CAN (mole × 10^{-4})	Time (min)	% Grafting	Intrinsic viscosity (dL/g)	Mol. wt. (g/mole)	Radius of gyration (R_z)
Synthetic details of optimized grades of microwave assisted synthesis (amount of polysaccharide = 0.0061 in each synthesis)							
TKP-g-PAM (MA)	0.14	0.21	2	87	8.98	6.02×10^6	112.7
CMS-g-PAM (MA)	0.14	0.21	2	64	8.28	5.12×10^6	101.05
SAG-g-PAM (MA)	0.21	0.21	2	54	12.9	8.66×10^4	98.4
Rishfloc 226 LV	–	–	–	–	–	4.84×10^6	93.2



Scheme 1. Schematic representation for the synthesis graft copolymer using conventional, microwave initiated and microwave assisted method.

2.3. Characterization

2.3.1. Intrinsic viscosity measurement

Viscosity measurements of the polymer solutions were carried out with an Ubbelohde viscometer at 25 °C. The viscosities were measured in 1 (M) sodium nitrate ($NaNO_3$) solution. The pH of the solution was neutral. The time of flow for solutions was measured at four different concentrations. The intrinsic viscosity was calculated by plotting η_{sp}/C versus C and $\ln \eta_{rel}/C$ versus C and then taking the common intercept at $C = 0$ of the best fitted straight lines from the two sets of points as described earlier (Rath & Singh, 2000). The intrinsic viscosity of the graft copolymers has been reported in Table 1.

2.3.2. Determination of weight average molecular weight and radius of gyration by SLS analysis

The weight average molecular weight (M_W) and radius of gyration (R_z) of polysaccharides and various grades of grafted polysaccharides were determined by static light scattering (SLS) analysis using Light Scattering Spectrophotometer (Model Nano ZS made by Malvern Inst., UK). Their values have been summarized in Table 1.

2.3.3. Elemental analysis

The elemental analysis of polysaccharides (CMS = % C – 32.11, % H – 8.81, % N – 0.00; TKP = % C – 44.15, % H – 10.05, % N – 2.27; SAG = % C – 36.50, % H – 4.00, % N – 0.40), polyacrylamide (% C – 50.80, % H – 7.69, % N – 19.76) and optimized grades of grafted polysaccharides (CMS-g-PAM = % C – 41.28, % H – 7.45, % N – 9.88; TKP-g-PAM = % C – 45.90, % H – 9.46, % N – 9.89; SAG-g-PAM = % C – 41.00, % H – 5.10, % N – 7.50) was undertaken with an Elemental Analyzer (Make – M/s Elementar, Germany; Model – Vario EL III).

2.3.4. Scanning electron microscopy (SEM)

Surface morphology of polysaccharides, polyacrylamide and polyacrylamide grafted polysaccharides were analyzed in scanning electron microscopy (SEM) in powdered form (Model: JSM-6390LV, Jeol, Japan) (Fig. 1).

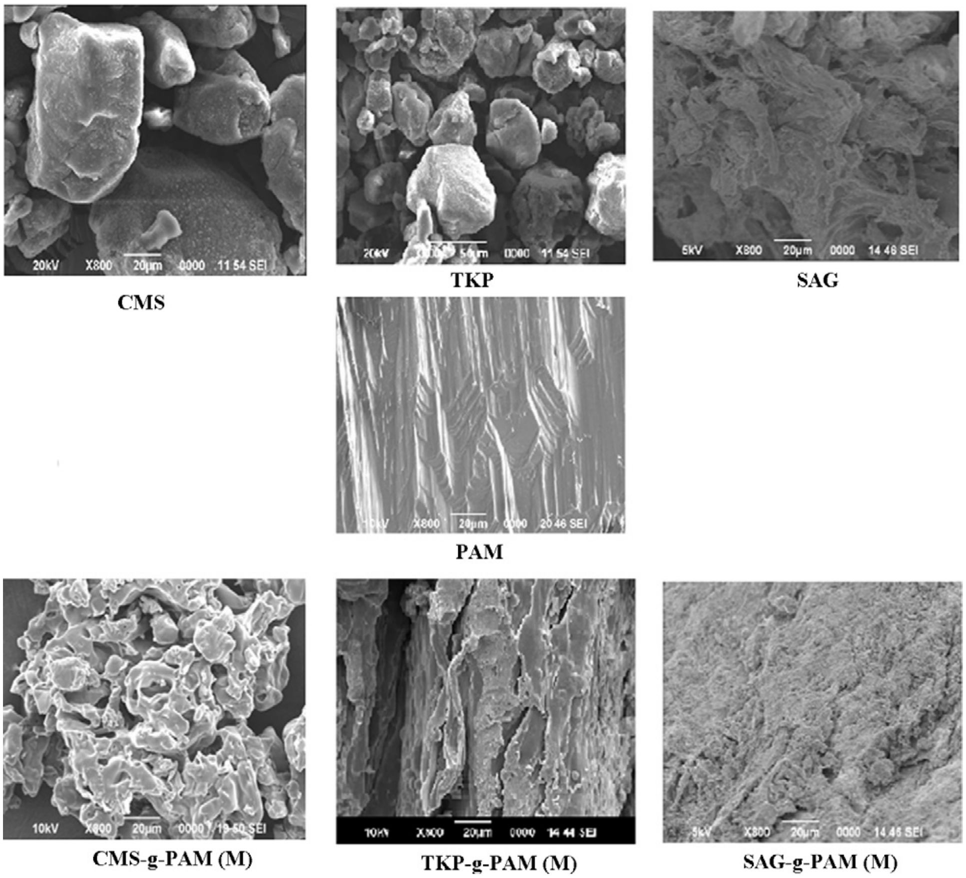

CMS
TKP
SAG
PAM
CMS-g-PAM (M)
TKP-g-PAM (M)
SAG-g-PAM (M)

Fig. 1. Scanning electron microscopy of polysaccharides, PAM and polyacrylamide grafted polysaccharides.

2.4. *Flocculation studies*

2.4.1. *Investigation of flocculation characteristics in synthetic wastewater (kaolin suspensions)*

The flocculation efficiency of various polymeric flocculants was determined using standard jar test method.

A conventional jar test method is comprised of a flocculator and a turbidity meter. The flocculator was supplied by Simeco, Kolkata, India and the turbidity meter was procured from Systronics, Ahmedabad, India. The flocculator consists of six equal size pedals on a bench, connected to each other by a gear mechanism. The flocculator has a provision of speed control. 0.25 wt% suspensions of kaolin (prepared by mixing 1 g in 400 mL of distilled water) were used for flocculation study. The suspensions were taken in each of four 1-L beakers and the flocculants were added in solution form. The following procedure was uniformly applied – immediately after the addition of flocculant; the suspension was stirred at a constant speed of 50 rpm for 5 min. The flocs were then allowed to settle down for 15 min. At the end of the settling period, the turbidity of the supernatant liquid was measured. The turbidity is expressed in Nephelo Turbidity Unit (NTU). The flocculants concentration was varied from 0.025 to 0.5 ppm, calculated with respect to the total weight of the solution. The relationship between polymer concentration and residual turbidity of the supernatant liquid are plotted in Figs. 2–5.

2.4.2. *Applications of polyacrylamide grafted polysaccharides as flocculants for the treatment of municipal sewage wastewater*

It is well known that municipal sewage wastewater constitutes an important part of the total wastewater from various sources. Proper treatment of municipal sewage wastewater becomes top priority enforcement in recent years. Flocculation is an important phenomenon for purification of municipal sewage wastewater for its reuse, as it can decrease the total pollutant content from the wastewater.

To find out the effectiveness of the laboratory synthesized graft copolymers as flocculants for the treatment of municipal sewage wastewater, following experiments were carried out.

The experiment was carried out in various sets. In the control set, 400 mL of the municipal sewage wastewater was stirred for 5 min, at 50 rpm, then left to settle for 15 min. At the end of settling

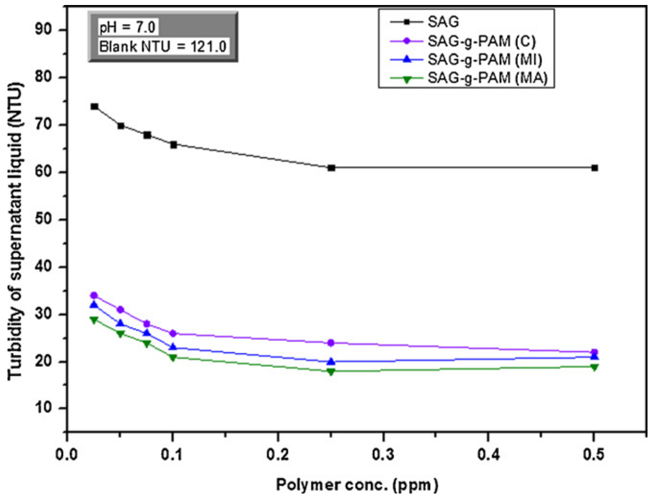


Fig. 2. Jar test result in 0.25 wt% kaolin suspension using SAG-g-PAM synthesized by various methods.

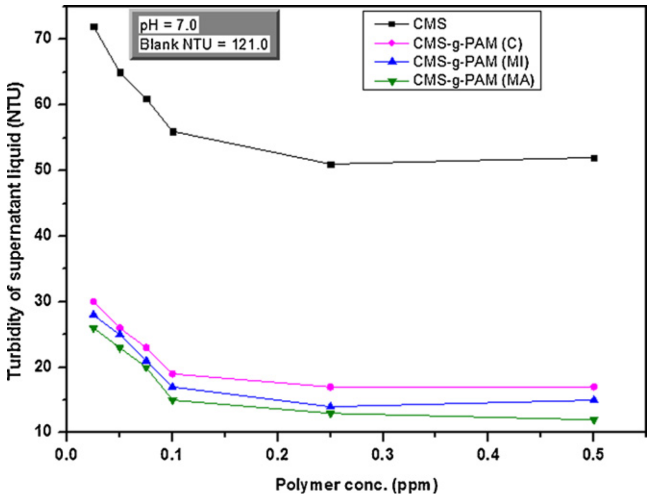


Fig. 3. Jar test result in 0.25 wt% kaolin suspension using CMS-g-PAM synthesized by various methods.

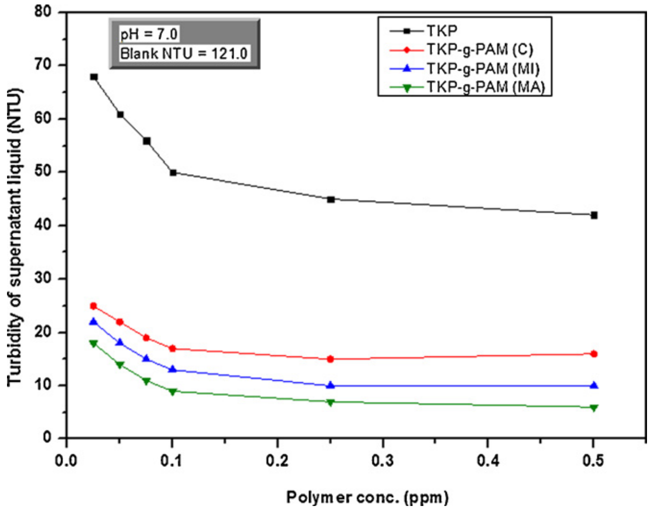


Fig. 4. Jar test result in 0.25 wt% kaolin suspension using TKP-g-PAM synthesized by various methods.

period, supernatant liquid was drawn from its top layer. The result of analysis from this control batch determines the inherent (natural) settling ability of the wastewater (i.e. the results from this batch act as a baseline with respect to which the efficiency of the graft copolymers has been determined).

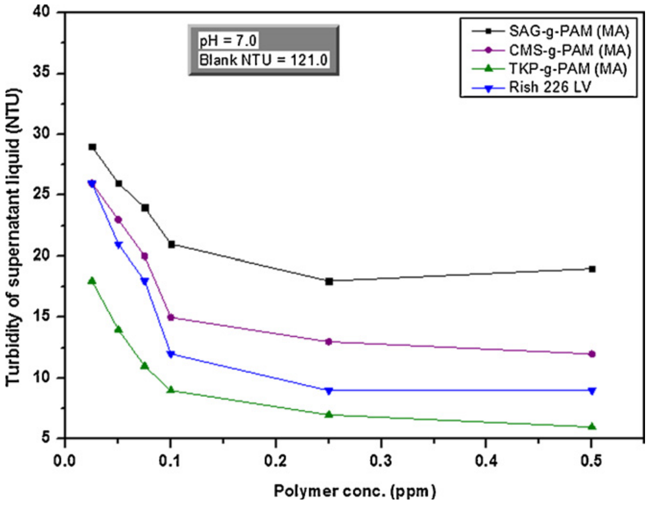


Fig. 5. Jar test result in 0.25 wt% kaolin suspension using various laboratory synthesized graft copolymers and commercial flocculant.

Other sets also consisted of 400 mL of the same municipal sewage wastewater treated through the same procedure as above, but in presence of 9 ppm of various flocculants.

2.4.2.1. Chemical analysis of the supernatant liquids. The supernatant liquids drawn as described above, from various sets of experiments were subjected to the following chemical/environmental analysis:

(1) Turbidity testing using calibrated nephelo-turbidity meter (Digital Nephelo-Turbidity Meter 132, Systronics, India).
(2) Trace metal analysis for total iron, total manganese and total chromium; after nitric acid digestion (Greenberg, 1999) using Atomic Absorption Spectrophotometer (AAS) (AA-680, Atomic Absorption/Flame emission Spectrophotometer, Shimadzu Corporation, Japan).
(3) Total Nickel was estimated by spectrophotometric method (Greenberg, 1999), using visible spectrophotometer.
(4) Determination of Total Solid (TS), Total Dissolved Solid (TDS) and Total Suspended Solid (TSS) by gravimetric method (Greenberg, 1999).
(5) COD was determined by standard method (Greenberg, 1999).

The results of these analyses have been summarized in Table 2.

Table 2
Analysis result for the treatment of municipal sewage wastewater.

Flocculant	Turbidity (NTU)	TS (ppm)	TDS (ppm)	TSS (ppm)	COD (ppm)	Total Fe^{3+} (ppm)	Total Mn^{2+} (ppm)	Total Cr^{2+} (ppm)	Total Ni^{2+} (ppm)
Without flocculant (blank)	58	600	265	335	540	5.35	1.8	0.786	0.91
CMS	57	545	235	310	470	4.8	1.2	0.66	0.80
CMS-g-PAM (C)	40	475	230	245	305	3.72	0.84	0.30	0.41
CMS-g-PAM (MI)	31	365	210	155	260	1.42	0.02	0.00	0.06
CMS-g-PAM (MA)	22	285	205	80	240	0.24	0.012	0.00	0.00
TKP	55	525	232	293	455	4.76	1.08	0.444	0.73
TKP-g-PAM (C)	37	460	220	240	285	3.21	0.096	0.276	0.42
TKP-g-PAM (MI)	28	355	210	145	246	1.14	0.023	0.029	0.08
TKP-g-PAM (MA)	**14**	**260**	**205**	**55**	**205**	**0.19**	**0.00**	**0.00**	**0.00**
SAG	59	550	240	310	485	4.92	1.44	0.7	0.83
SAG-g-PAM (C)	44	490	235	255	324	3.9	1.02	0.44	0.66
SAG-g-PAM (MI)	34	370	225	145	295	2.56	0.034	0.04	0.062
SAG-g-PAM (MA)	24	305	215	90	254	1.05	0.022	0.00	0.00
Rishfloc 226 LV	21	305	210	95	220	0.87	0.019	0.022	0.042

3. Results and discussions

3.1. Synthesis

Polyacrylamide grafted polysaccharide has been synthesized by conventional method using ceric ammonium nitrate as a free radical initiator in an inert atmosphere of nitrogen.

The most widely used method of chemical initiation for graft copolymerization onto polysaccharides has been with ceric salts like ceric ammonium nitrate (CAN) or ceric ammonium sulfate (CAS). The mechanism by which Ce(IV) generates free radical is believed to involve the formation of a chelate complex between the hydroxyl group of the polysaccharide and the oxidant. Afterwards, the complex disproportionates forming free radicals on the polysaccharide backbone. These active free radical sites in the presence of acrylic monomers generate graft copolymers.

Grafted polysaccharides have also been synthesized by using microwave initiated (only microwave irradiation to generate free radical sites) and microwave assisted method (using microwave energy as well as free radical initiator to generate free radical sites). The optimized grade has been obtained through its higher percentage of grafting, higher intrinsic viscosity and higher molecular weight (Ghosh, Sen, Jha, & Pal, 2010; Sen et al., 2009; Sen, Singh, & Pal, 2010).

When small polar molecules like water are irradiated with microwave, it results in rotation of the molecules, leading to generation of heat. However, no free radical is produced as such. However, if bigger molecules or macromolecules are present, rotation of the entire molecule is not possible. In that case, the microwave is absorbed by the polar groups present (e.g. –OH groups attached to polysaccharide backbone) and consequently, the severing of bond took place, leading to formation of free radical sites. Further, the microwave energy absorbed by the water molecules is quickly transferred to the acrylamide molecules, causing dielectric heating, which results in severing of the double bonds; thus producing another set of free radicals. The microwave is also known for lowering Gibbs energy of activation of the reaction (Galema, 1997). These effects generate the free radicals on the polar –OH groups of the polysaccharide backbone and on the monomer; the free radicals thus created then recombined with each other through initiation, propagation and termination steps to produce the graft copolymer.

3.2. Characterization

The intrinsic viscosity was evaluated for polysaccharides and the optimized grade of polyacrylamide grafted polysaccharides as reported in Table 1. It is well known that the intrinsic viscosity of polymer is a measure of its hydrodynamic volume in solution, which in turn, is a function of the polymer molecular weight, its structure, the nature of the solvent and the temperature of the medium. Among a series of polymers, the polymer having longer branches will have higher intrinsic viscosity and vice versa. It is obvious that the intrinsic viscosities of the entire grafted products are higher compared to the base polysaccharide. This is because of the presence of grafted PAM chains onto the polysaccharide backbone which results in the higher molecular weight as well as higher radius of gyration i.e. higher pervaded volume.

It is being observed that grafted products have higher molecular weight as well as higher radius of gyration compared to base polysaccharide (Table 1). This is because of the presence of grafted polyacrylamide chains onto the polysaccharide backbone. Among graft copolymers based on carboxymethylstarch (CMS), tamarind kernel polysaccharide (TKP) and sodium alginate (SAG) synthesized by three different methods, TKP-g-PAM (MA) is having highest molecular weight as well as radius of gyration and hence it is being assumed that as a flocculant it should be superior, as the case here (Fig. 5).

From elemental analysis result, it has been observed that graft copolymers are having considerable percent of nitrogen in comparison to polysaccharide, which confirms that PAM chains have been grafted on the backbone of polysaccharide.

It has been found from the SEM micrographs of polysaccharides and their grafted products (Fig. 1) that profound morphological changes have been taken place in form of transition from granular to fibrillar structure. This is because of the fact that, grafted polyacrylamide chains are agglomerated and converted to fibrillar morphology.

3.3. Flocculation characteristics

3.3.1. Flocculation characteristics in kaolin suspensions

The flocculation characteristics of various graft copolymers synthesized by different methods were compared in 0.25 wt% kaolin suspensions. The results are summarized in Figs. 2–4. In each case, the turbidity of the supernatant liquid after flocculation was plotted against polymer concentration. It is obvious from these figures that the flocculation performance of the optimized grade of graft copolymers synthesized by microwave assisted method showed the best flocculation efficiency followed by optimized graft copolymers synthesized by microwave initiated method and free radical initiated grafting method, respectively.

This is because of the highest percentage of grafting in case of microwave assisted method. Now, higher is the percentage of grafting, longer will be the grafted PAM chains and higher would be the molecular weight and radius of gyration. With increase in molecular weight and radius of gyration, the approachability of the contaminants towards the graft copolymer will be increased and hence better will be the flocculation efficiency as is the case here, in conformity with Singh's Easy Approachability Model (Singh, 1995; Singh, Karmakar et al., 2000; Singh, Nayak, Biswal, Tripathy, & Banik, 2003; Singh et al., 2009; Singh, Tripathy et al., 2000) and Brostow, Pal and Singh's model of flocculation (Brostow, Pal, & Singh, 2007). Further the flocculation characteristics of optimized grade of graft copolymers were compared with a commercial flocculant (Fig. 5) and it is interesting to note that laboratory synthesized graft copolymer [TKP-g-PAM (MA)] surpasses the flocculation characteristics of the commercial one. This is because of highly branched nature, higher molecular weight and radius of gyration of the TKP-g-PAM (MA) in comparison with other graft copolymers as well with commercial one. Consequently with increase in molecular weight, radius of gyration and branching, the approachability of the suspended particles towards the polymer increases and thus increasing the flocculation efficiency.

Earlier it was pointed out by Singh and co-workers (Brostow et al., 2007; Pal, Mal, & Singh, 2006; Singh, 1995; Singh, Karmakar et al., 2000; Singh et al., 2003; Singh, Tripathy et al., 2000) that graft copolymers of polysaccharides and polyacrylamide show synergistic effects in flocculation characteristics which was based on the premise that flexible polyacrylamide chains grafted on rigid polysaccharide backbones have easy approachability to contaminants in suspensions (Singh, 1995). It was observed that the higher the molecular weight and branching of polysaccharides better will be the flocculation characteristics (Adhikary, Tiwari, & Singh, 2007; Pal, Mal, & Singh, 2006). Brostow et al. (2007) presented a flocculation model relating the settling velocity with radius of gyration on the basis of Singh's Easy Approachability Model. The present results support the above.

The reason behind the microwave based synthesis giving better flocculants lies on the observation that in this synthesis, the chain opening of polysaccharide backbones does not take place; hence rigidity of the polysaccharide chain is maintained giving higher efficiency. However, highest grafting is obtained in microwave assisted synthesis where due to the synergism in grafting by ring opening under the free radical initiation and grafting without ring opening by microwave initiation provides the highest level of grafting as is evident from the molecular weight determination and flocculation characteristics presented here.

3.3.2. Application of synthesized graft copolymer as flocculant for the treatment of municipal sewage wastewater

Table 2 provides the results of treatment of municipal sewage wastewater with various flocculants. It clearly indicates that TKP-g-PAM (MA) considerably reduce the overall pollutant load (i.e. TS, TSS, TDS, COD, turbidity). Also, the total content of various metals are drastically reduced by using TKP-g-PAM (MA) as flocculant, in some cases (e.g. in case of total manganese, total chromium, total nickel), practically all of the metal got removed.

The role of surface charge is of prime importance in the application of flocculation. The surface charge influences the distribution of nearby ions in the liquid. Ions of opposite charge (counter-ions) are attracted towards the surface and ions of like charge (co-ions) are repelled away from the surface (Bratby, 2006). This, together with the mixing tendency of thermal motion and mutual ionic repulsion or attraction, leads to the formation of an *electric double layer* made up of the charged surface and a neutralizing excess of counter-ions over co-ions distributed in a diffuse manner in the nearby liquid. In our present case, all the flocculants described (i.e. CMS-g-PAM, SAG-g-PAM & TKP-g-PAM) here are nonionic or slightly anionic in nature. So, they have the advantage of being able to agglomerate colloids having low negative or slightly positive zeta potential value, which is the case here. However, among the graft copolymers based on CMS, SAG and TKP, TKP is having highly branched structure in comparison to others and hence is showing best flocculation efficacy.

4. Conclusions

From these observations, it can be concluded that highly efficient flocculants can be developed by using microwave assisted synthesis method.

Among various polysaccharide based graft copolymers, TKP-g-PAM (MA), which is having highest molecular weight and radius of gyration, is showing the best flocculation efficiency, which confirms Singh's Easy Approachability Model and Brostow Pal and Singh's Flocculation Model. Further, the best flocculant is achieved by microwave assisted synthesis followed by microwave initiated method and free radical initiation, respectively.

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