Carbohydrate Polymers 91 (2013) 294–299

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Amphoteric amylopectin: A novel polymeric flocculant

Ram Prakash Singh[a,*], Sagar Pal[b,**], Vijay Kumar Rana[a], Soumitra Ghorai[b]

[a] Indian Institute of Science Education and Research, 900, NCL Innovation Park, Dr. Homi Bhabha Road, Pune 411008, India
[b] Polymer Chemistry Laboratory, Department of Applied Chemistry, Indian School of Mines, Dhanbad 826004, India

ARTICLE INFO

Article history:
Received 30 May 2012
Received in revised form 25 July 2012
Accepted 8 August 2012
Available online 14 August 2012

Keywords:
Amphoteric
Amylopectin
Flocculation
Microwave processing

ABSTRACT

Novel flocculant based on amphoteric amylopectin for wastewater and industrial effluents treatment has been developed in authors' laboratory. Amphoteric flocculants have anionic and cationic moieties on the same macromolecule and is used to remove both positively and negatively charged contaminant particles in suspensions.

Amylopectin based flocculants have been found to be highly efficient flocculant and hence it has been chosen as base polysaccharide. By grafting of polyacrylamide and subsequent hydrolysis, anionic amylopectin has been synthesized. Afterwards, a cationic moiety has been inserted both by chemical/microwave processing. The flocculation efficiency of the amphoteric amylopectin has been tested in kaolin and iron ore suspensions. The results indicate its high efficiency in comparison with anionic, grafted, and base amylopectin. The amphoteric amylopectin prepared via microwave irradiation showed best flocculation efficiency.

1. Introduction

Polysaccharides are inexpensive, biodegradable, shear stable and low efficient flocculants. They are used at high doses in flocculation. On the other hand, polyacrylamide based flocculants used in wastewater and industrial effluent treatments are highly efficient at low doses, fragile and expensive. A new generation of flocculants has been developed by optimally grafting polyacrylamide branches on purified polysaccharide backbones in authors' laboratory at IIT Kharagpur (Brostow, Lobland, Pal, & Singh, 2009; Singh, Nayak, Biswal, Tripathy, & Banik, 2003; Singh, Pal, Krishnamoorthy, Adhikary, & Ali, 2009; Singh et al., 2000). These flocculants are synergistically efficient at low doses, controlled biodegradable, shear resistant, inexpensive and ecofriendly. Dangling polyacrylamide branches on rigid polysaccharides have easy accessibility to contaminants in suspensions (Singh's Easy Approachability Model, EAM) (Singh, 1995). The higher the molecular weight and degree of branching of polysaccharides, their graft copolymers show better flocculation efficiency. A flocculation model (Brostow, Pal, & Singh, 2007) has been developed which relates the sedimentation velocity of the contaminant particles and radius of gyration of polymeric flocculants, a measure of pervaded volume of polymers in suspensions. The grafted polysaccharides outperform most of the commercially available flocculants (Adhikary, Tiwari, & Singh, 2007; Singh et al., 2009; Tripathy, Karmakar, & Singh, 2001). Further, they have been hydrolyzed and cationized. All the three classes of anionic, non-ionic, cationic flocculants can be developed based on grafted polysaccharides. Earlier the grafting was performed by free radical solution polymerization technique. The experimental conditions were very stringent.

Recently it has been observed in authors' laboratory that graft copolymers synthesized by microwave initiated (using microwave irradiation alone to generate free radical on polysaccharides backbones) and microwave assisted (using microwave energy as well as ceric ammonium nitrate as initiator to generate free radical sites) methods provide better quality of graft copolymer with much higher percentage of grafting in comparison with conventional grafting method providing better flocculants (Pal, Sen, Ghosh, & Singh, 2012; Sen, Singh, & Pal, 2010).

A detailed comparative study has been performed on grafted carboxymethylstarch (CMS-g-PAM) (Sen, Kumar, Ghosh, & Pal, 2009), sodium alginate (SAG-g-PAM) (Sen et al., 2010), tamarind kernel polysaccharide (TKP-G-PAM) (Ghosh, Sen, Jha, & Pal, 2010) synthesized by free radical grafting, microwave initiated grafting and microwave assisted grafting method. The microwave assisted grafting method gives the best flocculation efficiency in all cases.

Amphoteric flocculants have been developed recently for their multiple applications (Jiang, Qi, Wang, & Tian, 2010; Yang et al., 2011; Zhang, 2001). The graft copolymers based on amylopectin provide the best performance (Rath & Singh, 2000). Hence this polysaccharide has been chosen for present study. By grafting and hydrolysis, first anionic moiety has been installed on amylopectin

---

* Corresponding author. Tel.: +91 9420482405.
** Corresponding author. Tel.: +91 326 2235769; fax: +91 326 2296615.
E-mail addresses: singh.prakash.ram@gmail.com (R.P. Singh), sagarpal1@hotmail.com (S. Pal).

0144-8617/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2012.08.024

Table 1
Characteristics of colloidal suspensions.

Suspension	Particle size (nm)	Zeta potential (mV) at neutral pH	Specific gravity (g/cc)
Iron ore suspension	95.8	−30.25	3.25
Kaolin suspension	82.5	−4.60	2.80

and then a cationic moiety has been chemically loaded on anionic amylopectin both by conventional and microwave processing. The flocculation efficiency of the amphoteric amylopectin has been tested in kaolin and Fe-ore suspensions. It is demonstrated that amphoteric amylopectin synthesized by microwave assisted process provides the best efficiency in flocculation.

2. Experimental

2.1. Materials

Amylopectin was purchased from Fluka Biochemica, Switzerland. Acrylamide and ceric ammonium nitrate were obtained from Merck, India. *N*-3-Chloro-2-hydroxypropyl trimethyl ammonium chloride (CHPTAC) was purchased from Lancaster, UK. Analytical grade of acetone and hydroquinone were supplied by S.D. Fine Chemicals, Mumbai, India. All the chemicals were used as received, without further purification. Methylene blue was procured from Merck, India.

Kaolin was supplied by Jyoti Chemicals, Howrah, India. Iron ore was a gift sample from Tata Steel Co., Jamshedpur, India. The details of analysis of kaolin and iron ore suspensions have been reported in Table 1.

2.2. Synthesis

2.2.1. Synthesis of amylopectin grafted with polyacrylamide (AP-g-PAM) by microwave assisted method

The synthesis of polyacrylamide grafted amylopectin using ceric ammonium nitrate and microwave irradiation has been accomplished as shown in Scheme S1a (Supporting Information). The optimization of synthetic parameters has been done. The amylopectin has been purified using ethyl alcohol by soxhlet extraction at reflux for 48 h. The synthesis details of AP-g-PAM are given in Table 2a.

2.2.2. Hydrolysis of the graft copolymer

The optimized grade of amylopectin based graft copolymer has also been completely hydrolyzed (Scheme S1b, Supporting Information). Table 2b provides the details of optimum hydrolysis. The reaction was carried out in open atmosphere, at 40 °C for 4 h in presence of 50 mL 1(N) NaOH, with a stirring speed of 400 rpm (water was used as solution medium). Finally the resultant product was precipitated in acetone.

2.2.3. Synthesis of amphoteric amylopectin

The optimally hydrolyzed graft copolymer was exhaustively cationized using N-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride (CHPTAC) by conventional method (Table 2c) as well as by microwave assisted method (Table 2d) (as shown in Scheme S1c, Supporting Information).

2.3. Characterization

Intrinsic viscosity measurements of the aqueous polymer solutions (pH = 7.0) of AP, AP-g-PAM, Hyd. AP-g-PAM, and amphoteric amylopectin were carried out using an Ubbelohde Viscometer with a capillary diameter of 0.58 mm at 25 °C. The C, H, N analysis was performed using an Elemental Analyzer (Perkin Elmer, Series-II, CHNS/O analyzer-2400). FTIR spectra were recorded in solid state

Table 2
Synthesis details of modified amylopectin.

a. Synthesis details of AP-g-PAM using microwave assisted method

Polymer grade	Amount of AP (mol)	Amount of AM (mol)	Amount of CAN (mol × 10^{-4})	Time (min)	Grafting efficiency (%)[a]
AP-g-PAM	0.0061	0.14	0.21	1.5	87.5%

b. Synthesis details of Hyd. AP-g-PAM

Polymer	Vol. of 0.1 (N) NaOH (ml)	Reaction time (h)	Reaction temp. (°C)	Neutralization equivalent (g)	Degree of hydrolysis[b]
Hyd. AP-g-PAM	50	3	60	437.70	43.41

c. Synthesis details of Amp. AP (C)

Polymer	Amount of Hyd. AP-g-PAM (g)	Amount of 1 (N) NaOH (ml)	Amount of CHPTAC (ml)	Time (min)	Temperature (°C)	Conversion (%)[c]
Amp. AP (C)	1	15	0.5	12	70	86.5

d. Synthesis details of Amp. AP (MA)

Polymer	Amount of Hyd. AP-g-PAM (g)	Amount of 1 (N) NaOH (ml)	Amount of CHPTAC (ml)	Time (min)	MW power	Temperature (°C)	Conversion (%)[d]
Amp. AP (MA)	1	15	0.5	1	900 W	70	92.8

[a] $\text{GE}(\%) = \frac{\text{wt. of graft copolymer} - \text{wt. of polysaccharide}}{\text{wt. of monomer}} \times 100.$

[b] $\text{Degree of hydrolysis} = \frac{\%\ \text{O in hydrolyzed product} - \%\ \text{O in unhydrolyzed product}}{\%\ \text{O in unhydrolyzed product}} \times 100.$

[c] $\text{Conversion}(\%) = \frac{\text{wt. of amphoteric} - \text{wt. of hydrolyzed product}}{\text{wt. of hydrolyzed product} + \text{wt. of CHPTAC}} \times 100.$

[d] $\text{Conversion}(\%) = \frac{\text{wt. of amphoteric} - \text{wt. of hydrolyzed product}}{\text{wt. of hydrolyzed product} + \text{wt. of CHPTAC}} \times 100.$

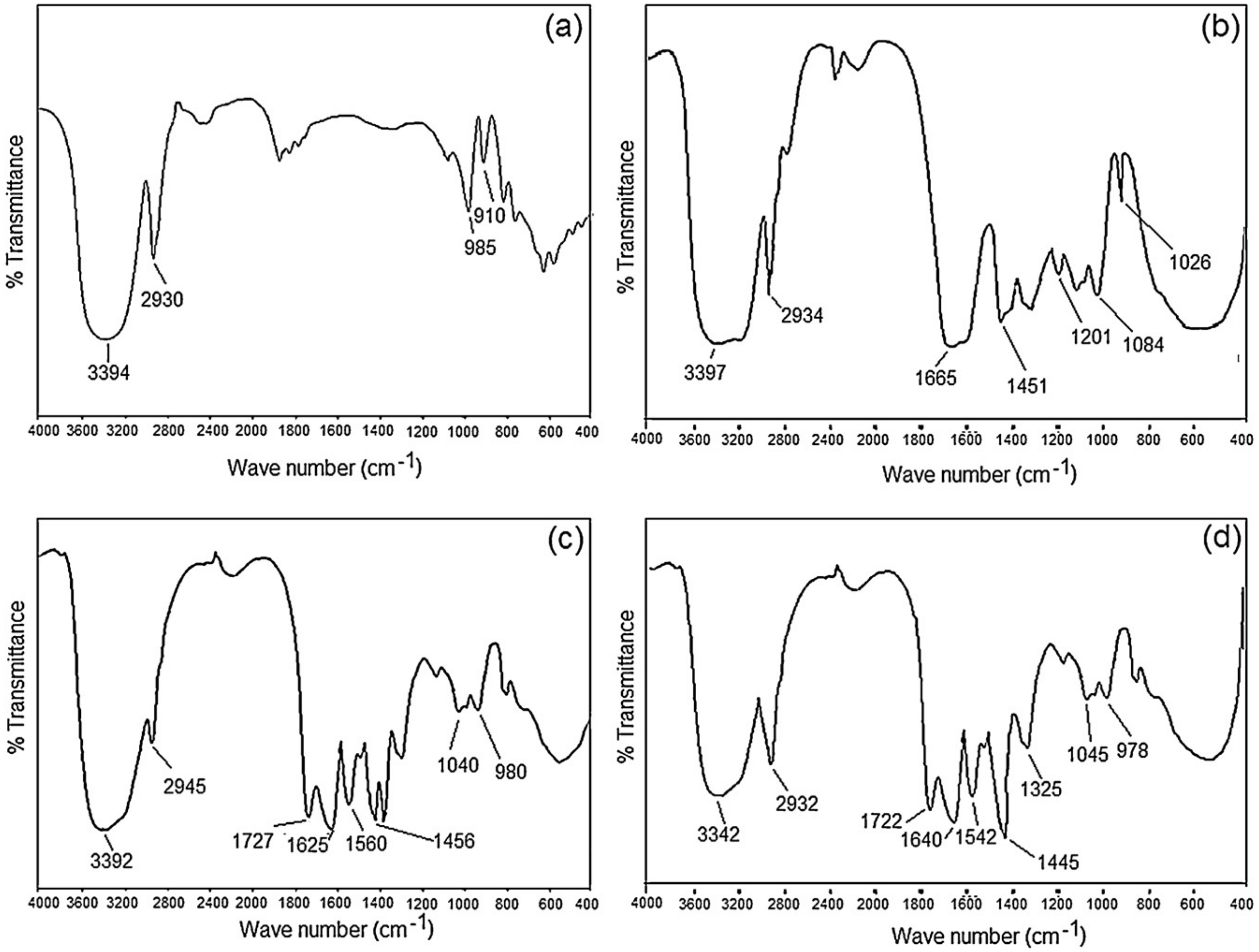

Fig. 1. FTIR spectra of (a) AP, (b) AP-g-PAM, (c) Hyd. AP-g-PAM, and (d) Amp. AP (MA).

using KBr pellets with a FTIR spectrophotometer (Model IR-Perkin Elmer, Spectrum 2000) between 400 and 4000 cm^{-1}. ^{13}C nuclear magnetic resonance (NMR) spectra were recorded in solid state using a 500 MHz Bruker Advance II-500 spectrometer.

2.4. Flocculation characteristics

2.4.1. Investigation of flocculation characteristics using sedimentation test

The flocculation characteristics of amylopectin, AP-g-PAM, Hyd. AP-g-PAM and Amp. AP were investigated in synthetic effluents (i.e. kaolin and Fe-ore suspensions) using column sedimentation test method. The details of test procedure are given in supporting information at the end of the text.

2.4.2. Flocculated decolourization of dye

The decolourization efficiency of methylene blue dye solution (0.001 wt%) was studied using AP, AP-g-PAM, Hyd. AP-g-PAM, and Amp. AP. Distilled water was used as reference. % Decolourization efficiency (% DE) (Pal, Ghorai, Dash, Ghosh, & Udayabhanu, 2011) was calculated using the following equation:

$$\%\text{DE} = \frac{A_0 - A}{A_0} \times 100 \tag{1}$$

where A and A_0 are the absorbances of the supernatant liquid after and before addition of flocculant, respectively. The details of test procedure are given in supporting information at the end of the text.

3. Results and discussion

Amphoteric amylopectin has been synthesized (Scheme S1, Supporting Information) by incorporating a cationic moiety using simple substitution reaction onto the backbone of hydrolyzed AP-g-PAM in conventional method (Table 2c) and microwave irradiation based method (Table 2d). It is evident that microwave based process provides higher conversion (%).

Fig. S1, Supporting Information indicates the intrinsic viscosities of amylopectin (Fig. S1a, Supporting Information), grafted amylopectin (AP-g-PAM) (Fig. S1b, Supporting Information), hydrolyzed grafted amylopectin (Hyd. AP-g-PAM) (Fig. S1c, Supporting Information) and amphoteric amylopectin (Amp. AP) (Fig. S1d). On grafting with PAM the intrinsic viscosity of graft copolymer increases which is further increased upon hydrolysis. This is because of the repulsion of electrostatic charges and consequent extension of branches. However by introducing cationic moiety on hydrolyzed grafted amylopectin, charge neutralization predominates. Consequently the extension of the branches is decreased resulting in smaller hydrodynamic volume i.e. lower intrinsic viscosity of the amphoteric amylopectin.

The elemental analysis of amylopectin, acrylamide, CHPTAC, grafted amylopectin (AP-g-PAM), hydrolyzed grafted amylopectin (Hyd. AP-g-PAM) and amphoteric amylopectin (Amphoteric AP) has been given in Table S1, Supporting Information. Closer scrutiny of concentrations of N, and O clearly indicates the presence of hydrolyzed and cationized moieties in amphoteric amylopectin, which is further confirmed by FTIR and ^{13}C NMR spectroscopy.

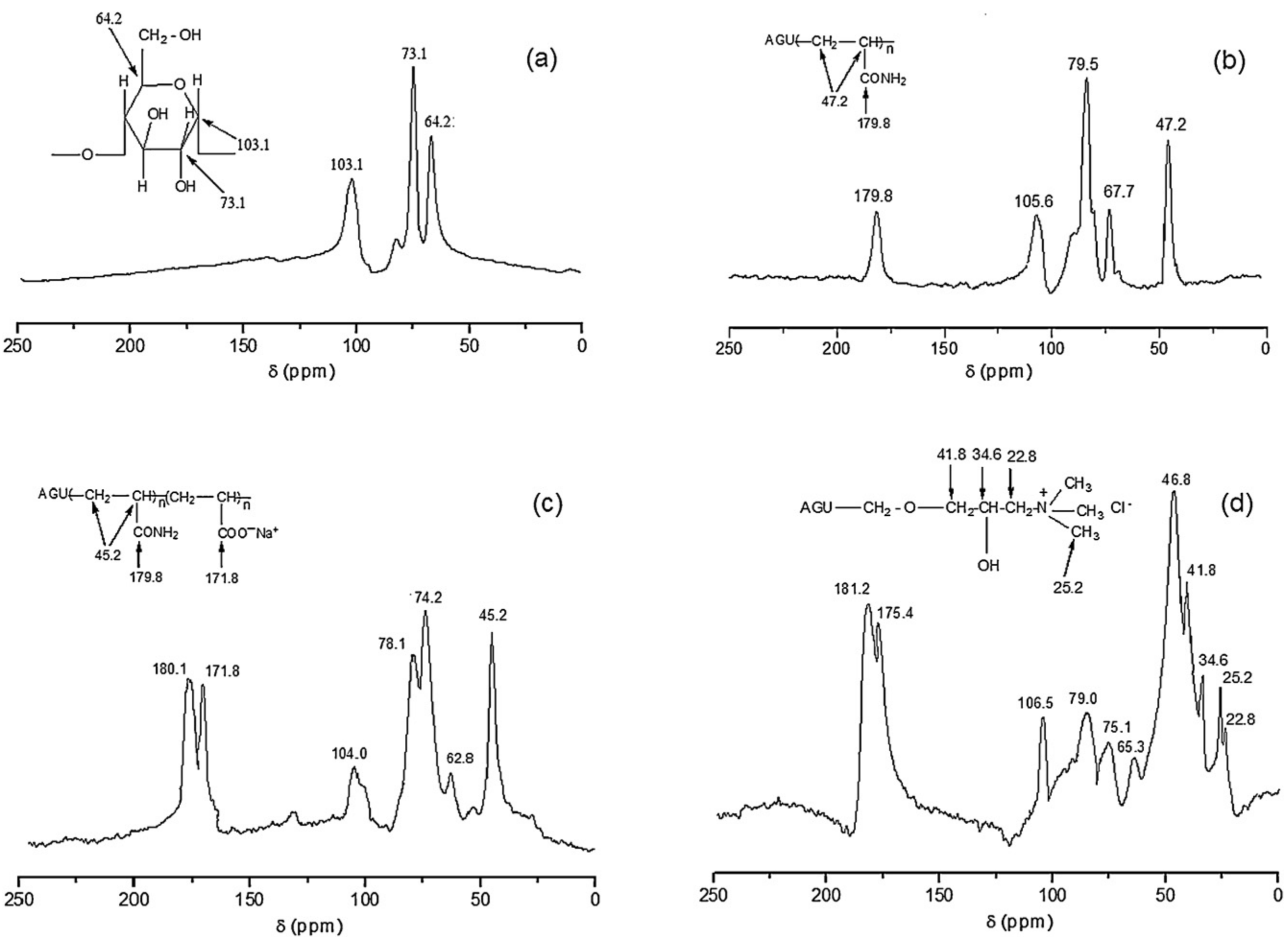

Fig. 2. ^{13}C NMR spectra of (a) AP, (b) AP-g-PAM, (c) Hyd. AP-g-PAM, and (d) Amp. AP (MA).

However, by comparing the % N content of Amp. AP synthesized by conventional and microwave based method, it is obvious that microwave based product has a higher nitrogen concentration, confirming the higher % of conversion.

From the FTIR spectrum of AP (Fig. 1a), it can be interpreted as follows: a broad peak at 3394 cm^{-1} is due to the stretching vibrations of O—H, a small peak at 2930 cm^{-1} attributed to the C—H stretching vibration. The bands at 985 cm^{-1} and 910 cm^{-1} are attributed to CH_2—O—CH_2 stretching vibrations. In case of AP-g-PAM (Fig. 1b), there are few additional bands present in comparison to AP. The band at 1665 cm^{-1} is attributed to C═O stretching vibration. One peak at 1451 cm^{-1} is for C—N stretching vibrations. The presence of these additional peaks confirms successful grafting PAM onto AP backbone. By comparing AP-g-PAM and Hyd. AP-g-PAM (Fig. 1c), there are two additional bands present in hydrolyzed product at 1727 cm^{-1} and 1560 cm^{-1}, which are assigned to —COO$^-$ group. The presence of these additional bands is a strong proof of hydrolysis of grafted polyacrylamide chains. In case of Amp. AP (MA) (Fig. 1d), there is no additional band present as such; however, the intensity of C—N stretching vibration (1445 cm^{-1}) is enhanced drastically. This is because of the —C—N of grafted PAM chains as well as —C—N stretching vibration of the inserted cationic moiety.

Amylopectin, AP-g-PAM, Hyd. AP-g-PAM, and Amp. AP (MA) were also characterized by NMR spectroscopy (Fig. 2). It is obvious from ^{13}C NMR spectrum of AP (Fig. 2a), that amylopectin has three distinct peaks. The absorption peak at $\delta = 103.1$ ppm is for anomeric carbon atom and the peak at $\delta = 73.1$ ppm is for carbon atoms connected by —OH groups (i.e. the carbon atoms in the six member ring except anomeric carbon atom) and another peak at $\delta = 64.2$ ppm is attributed to the carbon atom of a CH_2OH group. From the literature report (Pal et al., 2011) it is evident that the ^{13}C NMR spectrum of acrylamide has three major peaks. The peak at $\delta = 177.3$ ppm is from the amide carbonyl carbon. Peaks at $\delta = 130.5$ and 138.2 ppm are for two sp^2 hybridized carbon atoms (i.e. CH_2═CH—). In the ^{13}C NMR spectrum of grafted product (AP-g-APM) (Fig. 2b), there are two additional bands present, compared to AP. The presence of an intense peak at $\delta = 179.8$ ppm is because of carbonyl groups, along with an additional peak at $\delta = 47.2$ ppm which is attributed to a methylene group. This confirms that grafting of polyacrylamide chains onto AP backbone has been taken place. As obvious in the ^{13}C NMR spectrum of the graft copolymer and acrylamide, acrylamide had two peaks at $\delta = 130.5$ and 138.2 ppm for two sp^2 hybridized carbon atoms which were absent in the graft copolymer. Moreover, one additional peak was present for the graft copolymer at $\delta = 47.2$ ppm, which is for the sp^3 hybridized carbon atoms (i.e. $(—CH_2—CH—)_n$ units in the graft copolymer). Neither the AP nor the acrylamide spectrum had this peak. Therefore, the absence of peak at $\delta = 130.5$ and 138.2 ppm and the presence of a peak at $\delta = 47.2$ ppm is evidence of covalent attachment of the polyacrylamide chains onto the AP backbone. Further, by comparing the NMR spectra of AP-g-PAM and Hyd. AP-g-PAM (Fig. 2c), there is one additional peak present in case of later one at 171.8 ppm. This is for the carbon of carboxylate group, which clearly confirms that partial alkaline hydrolysis of the grafted PAM chains took place. However, by comparing the NMR spectra of Hyd. AP-g-PAM and Amp. AP (MA) (Fig. 2d), the presence of four additional peaks is a strong evidence of cationization onto Hyd. AP-g-PAM.

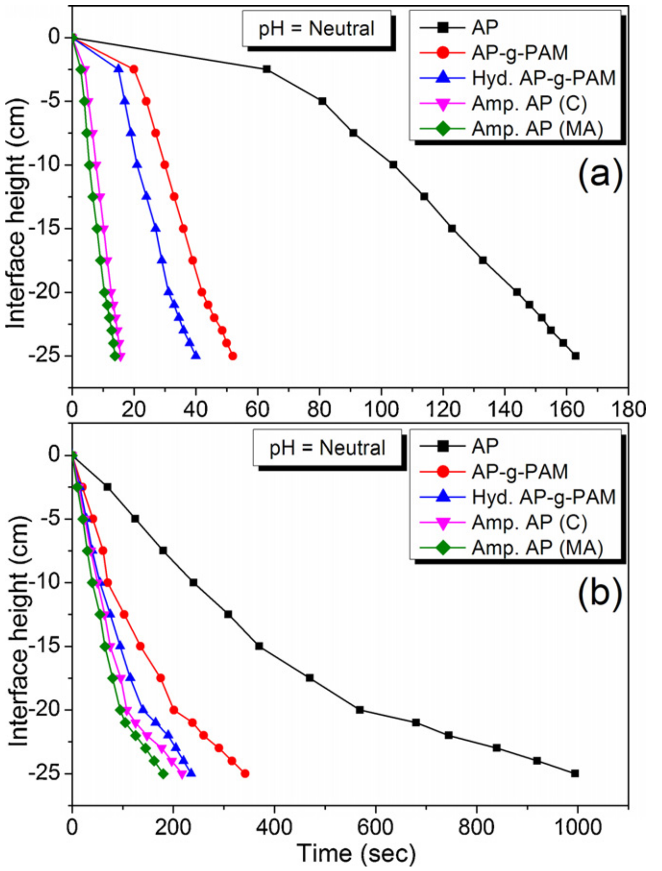

Fig. 3. Settling characteristics of (a) 5 wt% Fe-ore suspension and (b) 3 wt% kaolin suspension using AP, AP-g-PAM, Hyd. AP-g-PAM, Amp. AP (C) and Amp. AP (MA).

Fig. 3 depicts the flocculation performance of amylopectin and modified amylopectins in 5-wt% Fe-ore (Fig. 3a) and 3-wt% kaolin suspensions (Fig. 3b). It shows that the amphoteric amylopectin performs the best followed by hydrolyzed grafted amylopectin and grafted amylopectin in conformity with the Singh's Easy Approachability Model (EAM) (Singh, 1995) and Brostow et al.'s Flocculation Model (Brostow et al., 2007). The sedimentation rate (Table 3) also shows the same trend. However, by comparing the conventional way of synthesis and microwave irradiation based synthesis, it is obvious that microwave based Amp. AP shows the best flocculation efficacy, as per our expectation (Pal et al., 2012). Their efficacy was also estimated in removal of methylene blue dye (0.001-wt%) and the results are demonstrated in Fig. 4. As expected, the amphoteric amylopectin (Amp. AP) synthesized by microwave assisted method showed the best performance. This further indicates that the dye removal capability of Amp. AP (MA) is in conformity with the flocculation behaviour.

Table 3
Sedimentation rate of various flocculants.

Polymer	Sedimentation rate in Fe-ore suspension (cm/s)	Sedimentation rate in kaolin suspension (cm/s)
Without any flocculant	0.0091	0.0012
AP	0.139	0.035
AP-g-PAM	0.476	0.099
Hyd. AP-g-PAM	0.641	0.143
AMP. AP (C)	1.590	0.185
Amp. AP (MA)	1.920	0.210

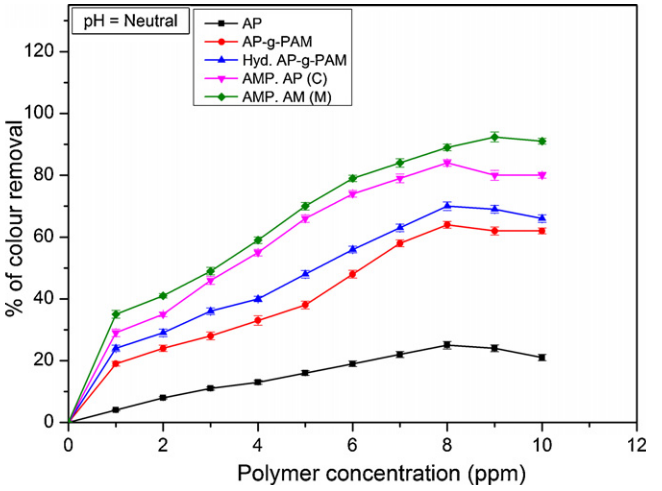

Fig. 4. % colour removal of methylene blue dye from aqueous solution using AP, AP-g-PAM, Hyd. AP-g-PAM, Amp. AP (C), and Amp. AP (MA) as flocculants. The results are mean ± SD ($n = 3$). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

4. Conclusions

Natural polymers mainly polysaccharides and synthetic (PAM) based polymers are used extensively as flocculants. The modified polysaccharides outperform existing flocculants in national and international markets. It has been proposed that polyacrylamide branches grafted on high molecular weight branched polymers have larger accessibility to contaminants in the suspensions (Singh et al., 2009). Recently it has been found that microwave assisted synthesis enhances the flocculation characteristics further (Pal et al., 2012). This is because of the synergism of free radical initiator and microwave irradiation, which makes the rigidity of polysaccharide chains unaffected. Amphoteric polysaccharides having anionic and cationic moieties on polysaccharide backbone are very efficient in suspensions of highly negative and positive contaminance. It also has applications in Shale Technology (which is a future applicable technology in oil/gas explorations). Here amphoteric flocculants have been successfully developed based on amylopectin using microwave assisted technique. Further, their efficiency has been demonstrated in moderately ionic (kaolin) and highly negative colloidal suspension (iron ore suspensions) and found that amphoteric amylopectin is the best flocculant.

Acknowledgements

The entire work reported in this paper was supported by CSIR Emeritus Scientist Scheme No. 21(0780)/09/EMRII. Authors express their gratitude to CSIR, New Delhi, India.

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.2012.08.024.

References

Adhikary, P., Tiwari, K. N., & Singh, R. P. (2007). Synthesis, characterization and flocculation characteristics of polyacrylamide grafted glycogen. *Journal of Applied Polymer Science*, *103*, 773–778.

Brostow, W., Lobland, H. E. L., Pal, S., & Singh, R. P. (2009). Polymeric flocculants for wastewater and industrial effluent treatment. *Journal of Materials Education*, *31*, 157–166.

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

Ghosh, S., Sen, G., Jha, U., & Pal, S. (2010). Novel biodegradable polymeric flocculant based on polyacrylamide-grafted tamarind kernel polysaccharide. *Bioresource Technology*, *101*, 9638–9964.

Jiang, X., Qi, Y., Wang, S., & Tian, W. (2010). New amphoteric flocculant containing beta cyclodextrin: Synthesis, characterization and decolourization. *Journal of Hazardous Materials*, *173*, 298–306.

Pal, S., Ghorai, S., Dash, M., Ghosh, S., & Udayabhanu, G. (2011). Flocculation properties of polyacrylamide grafted carboxymethyl guar gum (CMG-g-PAM) synthesised by conventional and microwave assisted method. *Journal of Hazardous Materials*, *192*, 1580–1588.

Pal, S., Sen, G., Ghosh, S., & Singh, R. P. (2012). High performance polymeric flocculants based on modified polysaccharides-microwave assisted synthesis. *Carbohydrate Polymers*, *82*, 336–342.

Rath, S. K., & Singh, R. P. (2000). Flocculation characteristics of grafted and ungrafted starch, amylose, and amylopectin. *Journal of Applied Polymer Science*, *66*, 1721–1729.

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

Sen, G., Singh, R. P., & Pal, S. (2010). Microwave initiated synthesis of polyacrylamide grafted sodium alginate: Synthesis and characterization. *Journal of Applied Polymer Science*, *115*, 63–71.

Singh, R. P. (1995). Advanced turbulent drag reducing and flocculating materials based on polysaccharides. In P. N. Prasad, J. E. Mark, & T. J. Fai (Eds.), *Polymers and other advanced materials, emerging technologies and business opportunities* (pp. 227–249). New York: Plenum Press.

Singh, R. P., Nayak, B. R., Biswal, D. R., Tripathy, T., & Banik, K. (2003). Biobased polymeric flocculants for industrial effluent treatment. *Materials Research Innovations*, *7*, 331–340.

Singh, R. P., Pal, S., Krishnamoorthy, S., Adhikary, P., & Ali, S. K. (2009). High technology materials based on modified polysaccharides. *Pure and Applied Chemistry*, *81*, 525–547.

Singh, R. P., Tripathy, T., Karmakar, G. P., Rath, S. K., Karmakar, N. C., Pandey, S. R., et al. (2000). Novel biodegradable flocculants based on polysaccharides. *Current Science*, *78*, 798–803.

Tripathy, T., Karmakar, N. C., & Singh, R. P. (2001). Development of novel polymeric flocculant based on grafted sodium alginate for the treatment of coal mine wastewater. *Journal of Applied Polymer Science*, *82*, 375–382.

Yang, Z., Shang, Y., Lu, Y., Huang, X., Chen, A., Jiang, Y., et al. (2011). Flocculation properties of biodegradable amphoteric chitosan based flocculants. *Chemical Engineering Journal*, *172*, 287–295.

Zhang, L. M. (2001). A review of starches and their derivatives for oilfield applications in China. *Starch*, *53*, 401–407.