



Novel cationic-modified salep as an efficient flocculating agent for settling of cement slurries

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ABSTRACT

A new cationic flocculant was synthesized by graft copolymerization of acrylamide (AM) and 3-(methacryloylamino)propyltrimethylammonium chloride (MAPTAC) onto salep using free radical polymerization initiated by ammonium persulfate (APS) to produce cationic salep [S-g-P(AM-co-MAPTAC)]. Reaction parameters (monomers/salep ratio, concentration of reactants, MAPTAC/AM ratio, and APS) were optimized using a full factorial experimental design to obtain the highest settling rate for cement suspensions. The best performing product was characterized by gel permeation chromatography (GPC), FTIR, ^1H NMR spectroscopy, and thermogravimetric analysis (TGA). The resulted cationic flocculant may be introduced as a promising candidate for the green production of asbestos-free fiber cement products by Hatschek process.

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1. Introduction

Flocculants play an indispensable role in many industries such as wastewater treatment, mineral processing, sludge dewatering, etc. (Haack, Heinze, Oelmeyer, & Kulicke, 2002; Oelmeyer, Krentz, & Kulicke, 2002). The aim of the flocculation process is to aggregate very fine, usually non settleable, particles to form larger and heavier mass for settling (Bratby, 2006).

A somewhat different application of flocculants, which has recently attracted the attention of many researchers, is the manufacture of eco-friendly fiber cement products by the Hatschek process (Blanco, Fuente, Alonso, & Negro, 2010; Coutts & Michell, 1983; Negro, Blanco, San Pio, & Tijero, 2007). While the chemical nature of asbestos makes it very compatible with cement, cellulose fibers behave in another way due to the differences in density, hygroscopic character, and chemical composition. Therefore, in the green process where the asbestos is replaced by cellulosic fibers, it is necessary to use a suitable flocculant to bind the fine cement particles to each other and to the fibers. This reduces the amount of fine material that passes through the film into the underflow and, as a consequence, enhances the overall efficiency of the process (Negro & Blanco et al., 2005).

Organic flocculants, such as polyacrylamide, poly (acrylic acid), and poly (styrene sulfonic acid) (Chen, Liu, & Wang, 2007) have widespread industrial application because they are effective in low dosages, they produce lower amounts of sludge, and their

molecular structure can be tailored to meet specific process requirements. The mechanism of action of organic flocculants is usually attributed to bridging between solid particles and formation of large flocs with a three-dimensional network structure (Tian, Wu, Liu, & Xie, 2010). However, other mechanisms such as hydrophobic association and electroneutralization can also be introduced by using a small number of hydrophobic, cationic, or anionic monomers in the polymer backbone (Negro, Sanchez, Fuente, Blanco, & Tijero, 2006; Chen et al., 2007).

Recently, many researches have focused on the usage of natural polymers such as polysaccharides as biodegradable, renewable, and cost effective materials for the synthesis of flocculants. Numerous reports describe the preparation of flocculants by introducing functional groups or by grafting polymers onto starch (Lin et al., 2012; Song, 2010; Song et al., 2009; Hao, Chang, Duan, & Zhang, 2007; Krentz et al., 2006; Jiang, Ju, Zhang, & Yang, 2010; Mishra, Mukul, Sen, & Jha, 2011). Modification of some other natural backbones such as, guar gum (Pal, Mal, & Singh, 2007), gum ghatti (Rani, Sen, Mishra, & Jha, 2012), and konjac glucomannan (Wang et al., 2011) are also reported to produce efficient flocculants. However, no reports regarding the application of salep in the synthesis of flocculants appears in the literature. Salep is a multi-component polysaccharide which is extracted from dried tubers of certain natural terrestrial orchids and is especially a good source of glucomannan (Fig. 1).

Salep is mostly known for its thickening, stabilizing, and flavoring effects in foods and drinks and has been the subject of a great deal of research (Yilmaz, Karaman, & Kayacier, 2013; Georgiadis et al., 2012; Dogan, Toker, & Goksel, 2011). Another major application of salep has been graft polymerization reaction with

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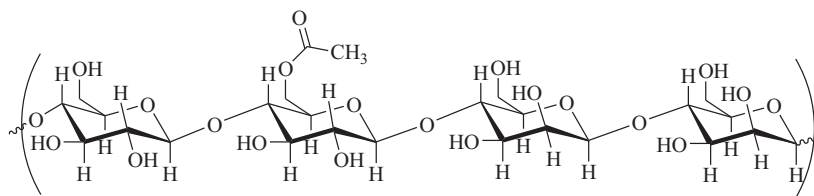


Fig. 1. Chemical structure of salep glucomannan.

acrylic monomers and crosslinkers (Pourjavadi, Soleyman, & Bardajee, 2008; Pourjavadi, Bardajee, & Soleyman, 2009), to produce hydrogels with different proposed applications ranging from carrier matrix for fertilizer release (Pourjavadi, Doulabi, Soleyman, Sharif, & Eghtesadi, 2012), and drug delivery (Bardajee, Hooshyar, & Kabiri, 2012), to smart materials and biosensors (Bardajee, 2011). There are a few works focusing on other applications such as preparation of water-soluble quantum dots (Bardajee, Hooshyar, Norouzi et al., 2012), and synthesis of silver nano-wedges (Pourjavadi & Soleyman, 2011).

In this study, cationic salep [S-g-P(AM-co-MAPTAC)] was synthesized for the first time as a new and efficient flocculant. It was demonstrated that the new flocculant is very efficient in settling cement particles and can be successfully applied in the production of green fiber cement composites.

2. Experimental

2.1. Materials and instruments

The palmate-tuber salep was purchased from a local supplier. Acrylamide and ammonium persulfate (both from Merck) were used without further purification. [3-(methacryloylamino) propyl] trimethylammonium chloride 50% solution in water (Sigma-Aldrich) was extracted with diethyl ether 5 times to remove inhibitor. Double distilled water was used in the synthesis of flocculant, and tap water used for the flocculation experiments. Tehran Portland Cement Type I (ASTM C150, 2004) was used for preparation of cement suspensions. The particle size analysis and the chemical and physical properties of the cement are presented (Supporting Information, Fig. S1 and Table S1).

^1H NMR spectra were taken by a Bruker DPX 500. FTIR spectra were recorded on an ABB Bomem MB-100 spectrophotometer. Thermogravimetric analysis (TGA/DTG) was performed on a TG209 instrument (NETZSCH). GPC measurements were carried out by using GPC-1100 Agilent technologies with refractive index detector and dextran as standard.

2.2. Synthesis of cationic salep

The reactions were carried out in a 250 mL reaction vessel equipped with mechanical stirrer, thermometer, and nitrogen gas inlet, and were heated using a thermostatic water bath. Salep was dissolved in water at 200 rpm and heated at 80°C under nitrogen for 30 min. Then the monomers were added and mixed for further 10 min to a homogeneous mixture. Ammonium persulfate was dissolved in 10 mL of water and added to the mixture and the reaction was continued for 15 min. The product was dewatered by ethanol and dried in a convection oven for 24 h at 50°C and then ground to pass through a 100-mesh sieve. Possible contaminations from nongrafted AM homopolymer or AM-co-MAPTAC copolymer were removed from the grafted polymers by extraction with a 1:1 vol. mixture of formamide and acetic acid.

2.3. Characterization methods

2.3.1. Molecular mass determination

The GPC instrument was equipped with a PL Aquagel-OH Mixed-H $8\ \mu\text{m}$ column and a differential refractive index detector. The mobile phase was water and the flow rate was 1 mL/min and acquisition interval was 0.43 s. Samples were prepared as 0.1% solutions in water, passed through a microporous filter with pore diameter of $0.45\ \mu\text{m}$, and 50 μL of the filtrate were injected in the sample loop.

2.3.2. Cationic charge density

The extent of incorporation of the cationic monomer in the graft copolymer was measured by Mohr titration. A 100 mL aliquot of 0.4% solution of purified salep-g-P(AM-co-MAPTAC) was titrated against 0.01 N AgNO_3 , using 2 mL of a 5% solution of K_2CrO_4 as indicator. A blank was determined by suspending a small amount of chloride free CaCO_3 in 100 mL of distilled water containing 2 mL of indicator solution.

2.3.3. ^1H NMR spectroscopy

^1H NMR spectra of salep, native salep-P(AM), and salep-g-P(AM-co-MAPTAC) were recorded at 500 MHz. About 30 mg of the oven-dried sample were added to 1 mL deuterium oxide ($>99.8\ \text{atom}\%$ D; Mesbah Energy, Tehran, Iran) in an NMR tube and dissolved by heating to 80°C and sonication.

2.3.4. FTIR spectroscopy

FTIR spectra were obtained from KBr pellets with a resolution of $4\ \text{cm}^{-1}$ in the range of $400\text{--}4000\ \text{cm}^{-1}$.

2.3.5. Thermogravimetric analysis

Samples of about 50 mg of dried powders were weighed into aluminum pans and were heated under a nitrogen atmosphere from 25 to 800°C at a heating rate of $10^\circ\text{C min}^{-1}$.

2.3.6. Settling rate

The efficiency of flocculants was evaluated on the basis of settling rates. A 100 mL graduated cylinder was filled with a suspension of cement in water and a specified volume of a 1000 ppm solution of flocculant was added. The cylinder was inverted 10 times for complete mixing and then was set upright. The required time for the frontier of settling bed to move from 90 mL to 30 mL mark (150 mm) was recorded by a stopwatch and the settling rates were calculated in mm s^{-1} .

3. Results and discussion

3.1. Synthesis of the cationic salep

Salep has a higher molecular weight (Pourjavadi et al., 2012) compared with other polysaccharides such as high amylose starch (Salemis & Rinaudo, 1984), carrageenan (Rochas, Rinaudo, & Landry, 1990), chitosan and alginate (Harding, Abdelhameed, & Morris, 2010). Since the efficiency of flocculants is closely related

Table 1
Experimental design for the synthesis of flocculant.

Sample code	Salep/water (wt.%)	Total monomers/salep (w/w)	MAPTAC/total monomers (mol%)	APS/salep (wt.%)	Settling rate vs. [flocculant] (mm/s) ^a	
					10 ppm	50 ppm
156	2	10	3	3	0.6	3.6
157	1	10	3	3	0.6	2.7
158	2	20	3	3	5	14.1
159	1	20	3	3	6.3	12.5
160	2	10	5	3	3.1	12.5
161	1	10	5	3	0.5	3.3
162	2	20	5	3	8.3	11.1
163	1	20	5	3	4.5	12.5
164	2	10	3	12	3.8	14.3
165	1	10	3	12	0.5	3.0
166	2	20	3	12	6.3	14.3
167	1	20	3	12	6.3	14.3
168	2	10	5	12	3.1	14.3
169	1	10	5	12	0.5	2.9
170	2	20	5	12	9.1	12.5
171	1	20	5	12	3.1	8.3
N ^b	2	20	0	12	0.2	<0.1
A ^c	2	20	5	12	<0.1	<0.1
NS ^d					0.5	0.5

^a Measured on a 6 wt.% cement in water slurry.

^b Salep-g-PAM (Neutral).

^c Salep-g-P(AM-co-AA) (Anionic).

^d Native salep.

to their high molecular weight (Song, 2010), therefore, we anticipated that choosing salep as backbone would be an effective means of achieving high molecular weight and efficient flocculants. The syntheses were performed according to the two-level full factorial experimental design (Table 1) to investigate the effect of the reaction parameters on the settling rate as a measure of performance of the product at different concentrations.

The analysis of results is represented in Fig. 2 as Pareto charts of effects. Pareto charts are effective statistical means of comparing the relative magnitude and the statistical significance of both main and interaction effects in which the absolute values of the standardized effects are shown in decreasing order. The red line at 2.571 serves as a reference and corresponds to an α -level of 0.05 which means that the risk of making a type I error (i.e. rejecting the null hypothesis when it is true) is only 5%. Therefore, any effect that extends past this red line is significant (at 95% confidence level).

Therefore, the first two important synthesis parameters were the weight ratio of total monomers/salep (B) and the salep/water wt.% respectively (A), regardless of the concentration of flocculant. The reason behind these observations is that increasing the ratio of total monomers/salep results in higher grafting levels and lengths, thus a higher molecular weight flocculant. Increasing the salep/water ratio enhances the meeting chances between salep and monomers, which results in more successful grafting of monomers onto salep. The third important synthesis parameter which controls the efficiency of the flocculant at lower concentrations (10 ppm) was the interaction between the salep/water wt.% (A) and the MAPTAC/total monomers mol% (C). In other words, increasing the amount of MAPTAC in the monomer feed was most effective when higher concentrations of salep/water were used. This can be understood by considering that the low meeting chances between MAPTAC (max. 5 mol% of total monomers) and AM or salep would be improved when the reaction medium is more concentrated. From the above observations, it became apparent that the cationic charge introduced to the flocculant by incorporation of MAPTAC plays an important role in flocculation, especially at low concentrations of flocculant. This could possibly be explained in terms of displacement of the already positive surface charge of cement particles toward more positive potentials by adsorption of flocculant molecules on the surface. This assumption was

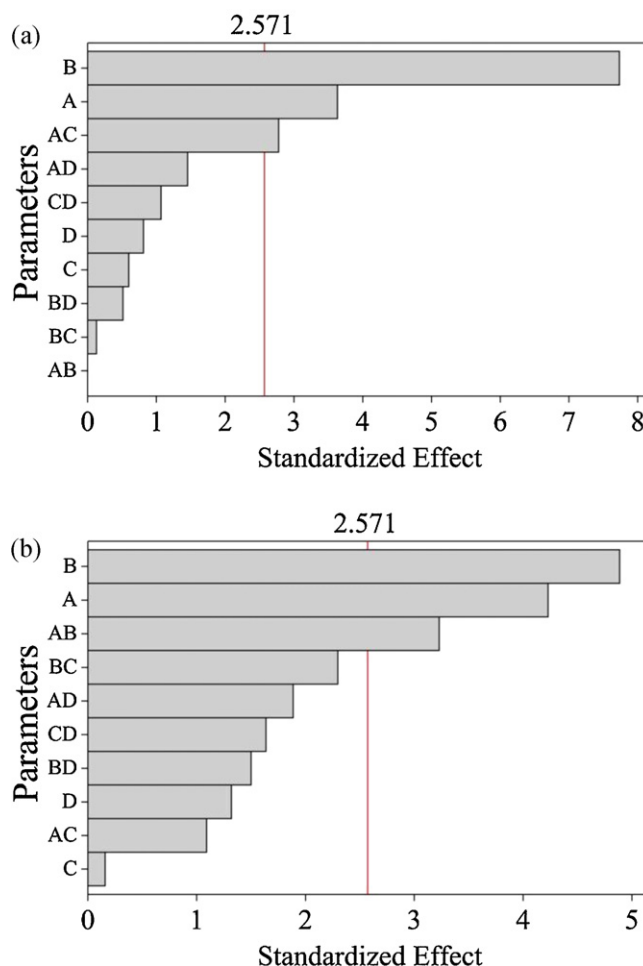


Fig. 2. Pareto charts for the main effects and interactions of synthesis parameters on the settling rate of salep-g-P(AM-co-MAPTAC) at 10 ppm (a), and 50 ppm (b). Parameters: salep/water wt.% (A), total monomers/salep w/w (B), MAPTAC/total monomers mol% (C), and APS/salep wt.% (D).

Table 2
Molecular weight characterization of salep and salep-g-P(AM-co-MAPTAC).

Sample	M_n	M_w	PDI
Native salep	1.17×10^6	1.64×10^6	1.39
Salep-g-P(AM-co-MAPTAC)	1.52×10^6	3.13×10^6	2.06

tested by synthesis of neutral and anionic samples (codes N and A, Table 1, respectively) based on the best performing formulation of cationic flocculant (code 170, Table 1), and comparing their settling rates with other samples. Evidently, these neutral and anionic graft copolymers could not be flocculants because they did not induce the formation of flocs. In fact, they could be considered as dispersants because they reduced the settling rate compared with the blank slurry (Supporting Information, Fig. S2). This observation provides further proof of the importance of electrostatic interactions in the efficiency of these flocculants. We also tried to make more efficient flocculants by increasing the MAPTAC/total monomers ratio, but all the products with more than 5 mol% of MAPTAC had inadequate solubility.

On the other hand, if the usage of flocculant at higher concentrations (50 ppm) is considered acceptable, then only the first two parameters (A and B) would be essential, because the third significant parameter was merely their interaction (AB). The reason why AC was not significant in this case could be that at higher concentrations of flocculant the bridging effect was dominant over the electrostatic interactions.

3.2. Characterization

Table 2 shows the results of molecular weight characterization of salep and sample 170 as the best performing salep-g-P(AM-co-MAPTAC). The weight average molecular weight (M_w) of the flocculant was nearly twice that of the native salep which confirms the efficiency of the grafting of monomers onto salep.

The cationic charge density of the flocculant was determined by Mohr titration. The average of three titrations indicated that 97% of the cationic monomer was grafted, which corresponds to a cationic charge density of 0.564 meq/g in the optimum sample.

Thermogravimetric analysis curves are shown in Fig. 3. The sharp weight loss (ca. 50%) for the native salep at 230 °C denoted the decomposition temperature of salep. The degradation of the cationic salep started at about the same temperature but proceeded more slowly up to 280 °C and then continued with a higher rate up to about 420 °C. This demonstrated the higher thermal stability of the cationic salep compared to native salep as a result of the grafting of monomers onto its backbone.

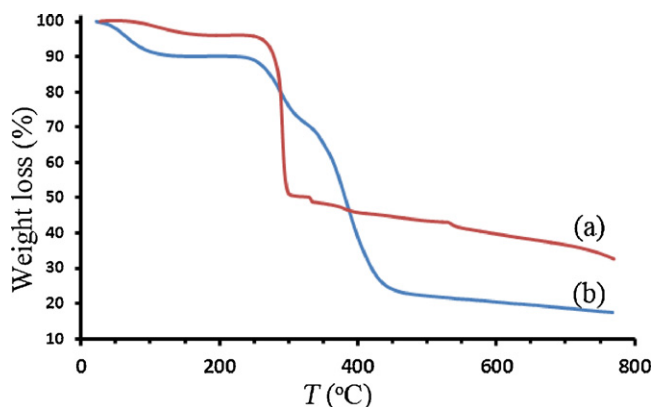


Fig. 3. TGA curves of salep (a) and salep-g-P(AM-co-MAPTAC) (b).

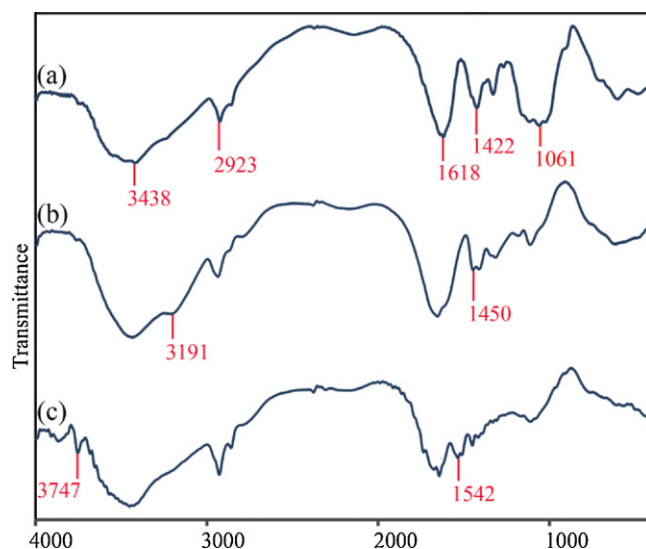


Fig. 4. FTIR spectra of salep (a), salep-g-PAM (b), and salep-g-P(AM-co-MAPTAC) (c).

FTIR spectra of native salep, salep-g-PAM and salep-g-P(AM-co-MAPTAC) are shown in Fig. 4. In the spectrum of salep, two strong peaks were observed at 1618 and 1422 cm^{-1} due to the asymmetric and symmetric stretching of ester groups in salep glucomannan. Characteristic absorption peak of salep appeared at 3438 cm^{-1} for the hydroxyl group and C–H aliphatic absorption peaks located at 2923 and 2860 cm^{-1} . The peaks at 1161, 1061 and 1022 cm^{-1} were assigned to asymmetric and symmetric stretching of ether linkage. In the spectrum of salep-g-PAM, the additional band at 1658 cm^{-1} corresponds to C=O stretching and the band at 1450 cm^{-1} to C–N stretching of amide groups.

In the spectrum of salep-g-P(AM-co-MAPTAC), the peaks at 1542 and 1517 cm^{-1} were attributed to N–H bending of mono substituted amide and the methyl groups of quaternary ammonium. Also, the stretching band of amide N–H of MAPTAC was observed at 3747 cm^{-1} which was absent in salep and salep-g-PAM.

The characteristic peaks in the ^1H NMR spectra of native salep, salep-g-PAM, and salep-g-P(AM-co-MAPTAC) are indicated in Fig. 5, which also supported the grafting of monomers to the salep backbone. The intensity of the characteristic peaks of AM and salep in the graft polymers were respective to their higher and lower concentrations in the formulation.

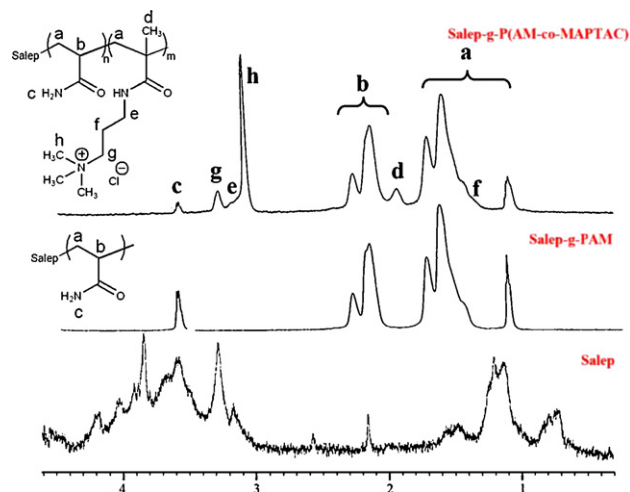


Fig. 5. ^1H NMR spectra of native salep, neutral salep and cationic salep.

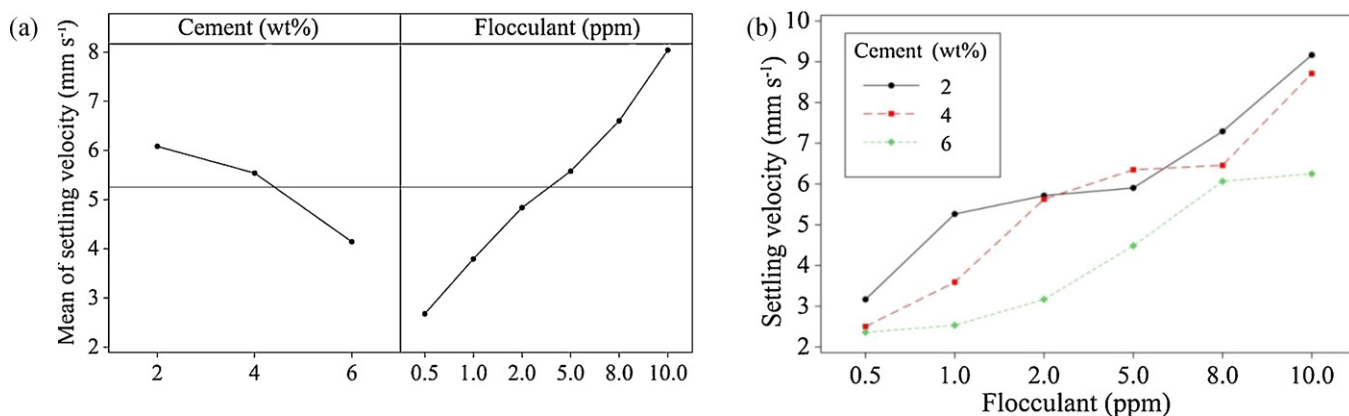


Fig. 6. Main effects plots (a) and interaction plots (b) of settling rate vs. concentrations of flocculant and cement.

Therefore, all characterization data, confirmed the successful grafting of the monomers onto the salep and formation of the cationic graft copolymer.

3.3. Settling rate

The settling rate of cement suspensions were investigated as a function of concentrations of cement and flocculant and the results were demonstrated in Fig. 6.

It was evident from the slopes of main effect plots, that the positive effect of concentration of flocculant on settling rate was much higher than the negative effect of cement concentration, and suggested that higher concentrations of cement could be simply settled by moderate addition in flocculant dosage. The interaction plots for cement concentrations of 2–4 wt.% were very close to each other and indeed they crossed at 2 and 6 ppm of flocculant which supported the above conclusion based on main plots. However, the settling rate of the 6 wt.% cement suspension was visibly lower, which indicated that the dosage of flocculant was insufficient to bring about effective flocculation of cement particles by either bridging or electrostatic effects; therefore, a higher dosage of flocculant was required.

In addition to the settling rate, we also tried to evaluate the efficiency of flocculants by means of visual comparison of the residual turbidity after 3 min from the start of settling of a 2 wt.% cement suspension with 50 ppm of flocculant (Supporting Information, Fig. S2). The 3 min delay was enough for the settlement of major part of cement in a blank suspension (without flocculant). Therefore, it made possible the comparison of efficiency of flocculants regardless of the rate of settling.

Evidently, under the above mentioned conditions, many of the cationic flocculants (156, 158, 160, 162, 164, 166, 167, 168) were as efficient as the best performing sample (170). A few samples (157, 159, 163, 165, 171) left more turbidity in the solutions and others (161, 169) were completely ineffective. The neutral (N) and anionic (A) samples were clearly dispersants rather than flocculants, since they left a more turbid solution compared with the blank sample. The qualitative analysis of these results proposed that the same synthesis parameters which control settling rate were again at work, albeit with a different order of importance: $A \gg B \sim C$. This means that in terms of residual turbidity, the worst practice in the synthesis of the flocculant would be a dilute reaction medium.

It is useful to compare the flocculation efficacy of salep-g-P(AM-co-MAPTAC) with other flocculants in settling of cement suspensions. However, this is not easy and straightforward because of the variety of techniques, instruments and conditions. For example, anionic, cationic, and neutral polyacrylamide were used in cement slurries with 5–10 wt.% concentration at an optimal dosage

of 100–200 ppm to achieve the best floc size in terms of chord length as measured by focused beam reflectance measurement (FBRM) system (Negro et al., 2006; Blanco et al., 2010). Other works also reported an optimum dosage of about 100 ppm which resulted in highest density and modules of rupture (MOR) of flocs (Negro, Blanco et al., 2005; Negro, Sanchez et al., 2005). Therefore, assuming that the highest settling rates in our work corresponded to best flocculation conditions in the above works, we conclude that salep-g-P(AM-co-MAPTAC) could be a more efficient flocculant with the much lower optimum dosage of less than 50 ppm for cement slurries with comparable concentrations.

4. Conclusion

A novel high molecular weight salep-g-P(AM-co-MAPTAC) was conveniently obtained by free radical polymerization in aqueous medium and successfully used as a cationic flocculant. Setting a combination of reaction parameters including salep/water, total monomer/salep, and MAPTAC/total monomer at their higher levels not only increased the settling rate at lower addition levels of flocculant but also improved the clarity of the solution at higher levels of addition. The importance of cationic charge for the performance of the flocculant at lower dosages suggested an electrostatic mechanism of flocculation rather than the bridging effect.

Compared with other cationic flocculants, the new salep-g-P(AM-co-MAPTAC) was more efficient and easier to prepare and it could be successfully used in Hatschek process for production of eco-friendly fiber-cement products.

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.2012.12.049>.

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