Carbohydrate Polymers 81 (2010) 317–322

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Flocculation efficiency of modified water soluble chitosan versus commonly used commercial polyelectrolytes

Rosana Rojas-Reyna[a,*], Simona Schwarz[a], Gert Heinrich[a], Gudrun Petzold[a], Sandra Schütze[a], Jörg Bohrisch[b]

[a] *Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Straße 6, D-01069 Dresden, Germany*
[b] *Fraunhofer Institut für Angewandte Polymerforschung, Geiselbergstr. 69, D-14476 Golm, Germany*

ARTICLE INFO

Article history:
Received 23 September 2009
Received in revised form
23 November 2009
Accepted 12 February 2010
Available online 7 March 2010

Keywords:
Flocculation
Clay dispersion
Chitosan
PolyDADMAC
Polyacrylamide

ABSTRACT

Aim of this work was to evaluate the flocculation efficiency of a modified, water soluble chitosan versus various commercial products such as: chitosan, PolyDADMAC and positively charged polyacrylamide. The flocculation properties were investigated in dispersions of the clay type "Blauton" by means of turbidity measurements, colloid titration and measurements of the floc size. It was found that flocculation occurs even before the Blauton surface charge neutralization is achieved. The modified chitosan was more effective than the commercial one in Blauton's settling. Modified chitosan in comparison to the commercial products demonstrated not only a wider flocculation window, but also a higher efficiency since lower amounts of polymer were required for the flocculation of Blauton. Finally, the use of modified chitosan resulted in an increase of the critical polymer concentration above which restabilization of Blauton occurs.

1. Introduction

Particles suspended in an aqueous medium have usually a net surface charge. The repulsive interactions, in spite of the Van der Waals forces trying to bring the particles together, stabilize the suspension. Aggregation of particles is fundamental for improving the performance of many solid–liquid separation processes. The efficiency of polyelectrolytes in such processes has led to their extensive application in the purification of drinking water, industrial raw and process water, municipal sewage treatment, mineral processing and metallurgy, oil drilling and recovery, paper and board production among others (Bolto & Gregory, 2007; Dautzenberg et al., 1994; Dragan, Maftuleac, Dranca, Ghimici, & Lupascu, 2002; Gregory, 1987; Tripathy & Rajan De, 2006).

The postulated mechanisms by which polyelectrolytes can bring about flocculation are charge neutralization, bridging and/or electrostatic patch (Bratby, 1980; Petzold, Mende, Lunkwitz, Schwarz, & Buchhammer, 2003; Petzold, Geissler, Smolka, & Schwarz, 2004). Charge neutralization leads to the reduction of the electric double layer between particles due to the adsorption of charged polyelectrolytes on oppositely charged particles. It is generally believed that polymers with low molecular weight tend to adsorb on and neutralize the opposite charges of the particles, while long-chain high molecular weight polymers can lead to bridging flocculation. In such cases, segments of a single polymeric chain are attached to more than one particle, thereby linking the particles together. The electrostatic patch flocculation resembles the concept of bridging, the main difference being the charge densities of the polymer and the particle. Low molecular weight polymers with high charge density, when interacting with oppositely charged particles of low charge density, lead to the formation of dense particle aggregations sharing the same polymeric chain, which can be visualised as a "polymeric patch". The main advantages of the use of polyelectrolytes instead of inorganic coagulants are: lower dose requirements, smaller volume of sludge, smaller increase in the ionic load of the treated water, and cost savings up to 25–30%. The main disadvantage of flocculation with polymers is the very small flocculation window, since even a small increase of the dosage can restabilize the system.

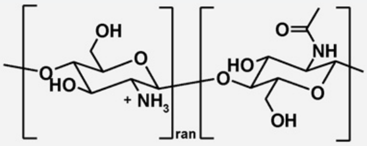
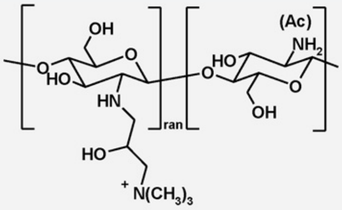
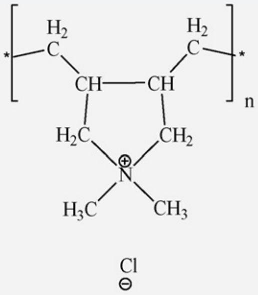
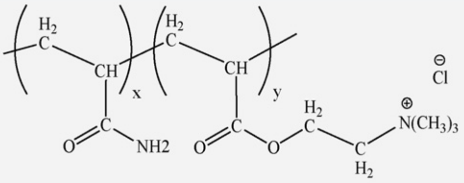
The importance of coupling polymer adsorption and flocculation of colloidal particles has been addressed in several papers (Bratby, 1980; Dautzenberg et al., 1994; Petzold et al., 2003; Rose & St. John, 1987) showing that adsorption of flocculants on dispersed solids is a process significantly affected by the charge density and the molecular weight of the polymer, the particle size distribution, the specific area, the solid content, and the mixing conditions. The structure

---

* Corresponding author at: Surface Modification, Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Straße 6, D-01069 Dresden, Germany.
Tel.: +49 351 4658 706; fax: +49 351 4658 231.
E-mail addresses: rojas@ipfdd.de, rozy_76@yahoo.com (R. Rojas-Reyna).

0144-8617/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2010.02.010

Table 1
Chemical structures of the polyelectrolytes used.

Sample	Structure
CH1: commercial chitosan	
CH2: modified chitosan	
PolyDADMAC	
PA: cationic modified polyacrylamide	

and charge of the adsorbed polymer layer determines whether the dispersed particles will be stabilized or aggregated and flocculated.

New and upcoming legislation on the use of synthetic polyelectrolytes for wastewater treatment has directed the investigations in this field towards the use of natural flocculants (Ashmore, Hearn, & Karpowicz, 2001; Bratskaya, Schwarz, Liebert, & Heinze, 2005; Bratskaya, Avramenko, Schwarz, & Philippova, 2006; Renault, Sancey, Badot, & Crini, 2009; Roussy, Van Vooren, & Guibal, 2005; Zeng, Wu, & Kennedy, 2008). Among the flocculants based on natural products, derivatives of chitosan and cationic starch (Bratskaya, Schwarz, Laube, et al., 2005; Bratskaya, Schwarz, Liebert, et al., 2005) are two of the most promising candidates for the replacement of synthetic polycations.

The main disadvantage of commercial chitosan products is their insolubility in water. These products must be dissolved, for instance, in acetic acid, and can therefore, be applied only within a small range of pH (up to about 7). At higher pH values precipitation occurs. The aim of this work was the comparison of the flocculation performance of a novel water soluble chitosan to commercial flocculants. The special clay type "Blauton" with a very high content of fine particles was used as model substrate.

2. Experimental

2.1. Materials

The water used in the present study was filtered via a Milli-Q Advantage A10 (18.2 mΩ cm at 25 °C).

2.1.1. Blauton

Blauton HFF-Spezial (Tonwerke Braun Witterschlick/Bonn) was used as received as model substrate for fine particles. Blauton is a mixture of minerals containing 60% Kaolinite, 25% Illite, 2% Montmorillonite and 13% Quartz.

2.1.2. Polyelectrolytes

In the present study the flocculation efficiency of chemically modified chitosan was compared to commonly used polyelectrolytes such as: commercial chitosan, PolyDADMAC and polyacrylamide (Table 1).

The commercial chitosan (CH1) with a molecular weight of approximately 400,000 g/mol was purchased from Heppe GmbH (Biotechnologische Systeme und Materialien) as flakes, with a deacetylation degree (DA) of 85%, ash content less than 1%, and was used without further purification.

The modified chitosan (CH2) with substitution degree of 0.77 and a DA of 85% was synthesized using a commercial, low viscosity chitosan by Fluka (MW 180,000 g/mol, polydispersity 2.1). 5 g (26 mmol) of the Fluka Chitosan were dispersed in 50 ml of water, the dispersion was heated at 60 °C. Thrice in 2.5 h intervals 4.22 g (83.5 mmol) of Glycidyl-trimethyl-ammonium chloride were added drop wise during continuous stirring. After 24 h at 60 °C the high viscosity product obtained is diluted and filtered. Finally, the product was extracted with 2 l of acetone, dialysed for 5 days (5 kDa) and lyophilised. The degree of substitution of CH2 (0.77) determined by ^{1}H NMR. The molecular weight of CH2 was calculated to be 305,500 g/mol.

PolyDADMAC (polyquat 40 U 50), with a molecular weight of 37,000 g/mol was purchased from Katpol Bitterfeld.

Cationic modified polyacrylamide (PA) (Praestol 644BC), with a molecular weight of 10^6 g/mol was supplied by Ashland, Germany.

2.2. *Methods*

2.2.1. *Preparation of Blauton dispersions*

1% (w/v) of Blauton was dispersed in water using a hand blender (300 W, Firma Braun) for 3 min followed by vigorous stirring during 1 h. The average size of Blauton particles in the dispersions at pH 6 was 2 μm as determined by means of the laser diffraction with a Mastersizer Microplus (Malvern Instruments, UK).

2.2.2. *Preparation of polyelectrolyte solutions*

A CH1 solution (1 g/l) was prepared by dissolving the chitosan flakes in a 1 vol.% acetic acid solution followed by intensive stirring for at least 48 h. The rest of the polyelectrolytes used were dissolved in deionized water under vigorous agitation ensuring the swelling of each flake.

2.2.3. *Flocculation*

The flocculation was studied via the “jar-test” using 50 ml of Blauton dispersions to which 100–1500 μl of polyelectrolyte solution was added. The samples were mixed via magnetic stirring for 15 min and allowed to sediment for 20 min. Finally, 10 ml of the supernatant were extracted for turbidity measurements using a 2100 AN turbidity meter (Hach).

2.2.4. *Floc size measurements*

The flocculated Blauton that resulted from the jar-tests was dispersed in water and the floc size was measured using a Malvern-Sizer laser diffraction particle size analyzer equipped with impeller mixer (rotation speed = 2000 rpm).

2.2.5. *Colloid titration*

Charge density measurements were conducted on polyelectrolyte solutions, Blauton dispersions as well as on flocculated Blauton using a PCD 03 Particle Charge Detector (Mütek GmbH, Germany) connected to a 702 SM Titrino potentiometric titrator (Metrohm, Switzerland). Solutions of sodium polyethylene sulfonate (PES-Na) or PolyDADMAC were used as titrants for cationic and anionic systems, respectively. Charge density (CD) (mequiv./g) was calculated according to the formula:

$$q = \frac{V \cdot c}{m}$$

where c is the titrant (PolyDADMAC or PES-Na) concentration (mequiv./l), V is the titrant volume, m is the content of polymer or substrate in the titrated solution (g).

Streaming potential–pH-profiles were measured with the same device.

3. Results and discussion

The flocculation efficiency of the used polyelectrolytes is determined by a variety of parameters among which are the pH range within which the flocculant is effective and the charge density of the polymer. The solution of CH1 demonstrates, as shown in Fig. 1, an isoelectric point at pH 7.3. On the other hand, CH2 and PA are positively charged over the whole pH range. Moreover, CH2 is soluble in water in contrast to unmodified chitosan (CH1) without addition of acetic acid. PolyDADMAC bearing quaternary groups is positive from pH 3 to 10 with a nearly constant charge density. The charge density of the flocculants at pH 6 decreases in the following order: PolyDADMAC > CH1 > CH2 > PA (Table 2). Zeta potential measurements, using a Malvern Instruments Zetasizer 3000, on Blauton dispersions demonstrate that the particles are negatively charged over the whole range of pH reaching a plateau at pH higher than 7 (Fig. 2).

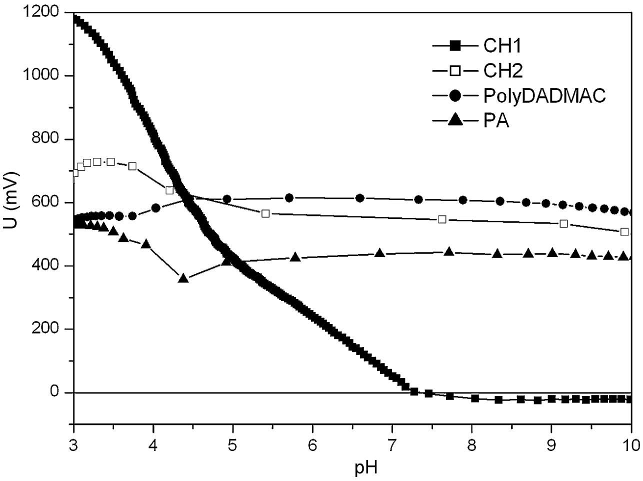


Fig. 1. Streaming potential–pH profile of polymers used.

Table 2
Charge density of the polymers used at pH 6.

Sample	CD (mequiv./g)
CH1	4.5
CH2	3.8
PolyDADMAC	7.6
PA	2.7

Blauton dispersions in water (10 g/l) were flocculated with the above mentioned polyelectrolytes. Turbidity measurements of the supernatant resulting from the jar-test versus the amount of polyelectrolyte used are shown in Fig. 3. PolyDADMAC and commercial chitosan CH1 demonstrate identical flocculation windows. In the case of PA a considerably high amount of polymer is necessary for the flocculation of Blauton, owing among others to the low charge density of the polymer, while in the investigated range no restabilization occurs. Finally, the optimum flocculation concentration of water soluble chitosan CH2 is within the range of the commercial products. Even if the amount required is higher than for CH1 the flocculation window is much broader; ranging from about 4 up to 12 mg/g.

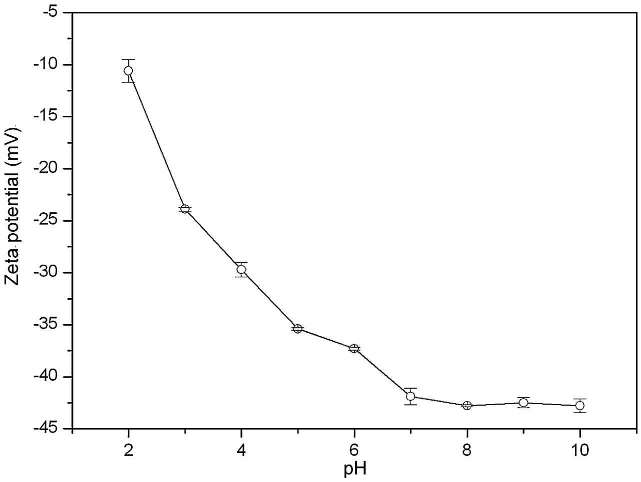


Fig. 2. Zeta potential–pH profile of Blauton.

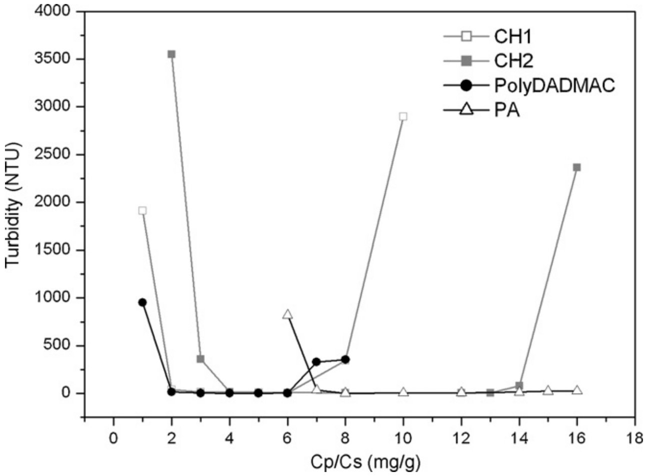


Fig. 3. Flocculation of Blauton dispersion (pH ~6, solid content 10 g/l).

The cationic charge and molecular weight of chitosan imply that it most probably flocculates Blauton via the charge neutralization mechanism. On the other hand, PolyDADMAC is a typical flocculant for both charge neutralization and/or patch flocculation. Even if high molecular weight is often mentioned as a required condition for bridging flocculation, the main factor that determines the mechanism to be followed is the charge density. Thus, polyelectrolytes with moderate or high charge density such as chitosan and PolyDADMAC flocculate mainly via charge neutralization or “charge patch” mechanisms even when the molecular weight is relatively high. In the case of polyacrylamide (PA) not only the molecular weight is extremely high (>10^6) but also the charge density was measured to be the lowest among the polyelectrolytes studied in this article. It is therefore safe to assume that it has most probably followed the bridging flocculation mechanism.

In Fig. 4 independent turbidity measurements of the supernatant collected after flocculating with CH2 are compared to the amount of titrant used to neutralize the supernatant’s charge. At low polymer concentrations the charge of the supernatant is negative due to non-flocculated Blauton particles. Increasing the amount of CH2 the turbidity drops dramatically and the supernatant is neutralized. Moderate increase of the polymer concentration (up to 12 mg/g of Blauton) does not affect the flocculation nor leads to a positive charge for the supernatant. CH1 and PolyDADMAC have demonstrated similar behaviour (data not shown) to that of CH2. On the contrary, in the case of PA the supernatant becomes positively charged at concentrations higher than 10 mg/g (Fig. 5). The wide concentration range, within which the supernatant of the sample with CH2 is neutral, is typical for charge neutralization or patch flocculation, where the charge density of the polymer is relatively high and a considerable fraction of the positive charges is not used for the particle’s neutralization. In such cases the chains of highly charge density can lead to a stable colloidal dispersion of positively charged particles. In the case of the

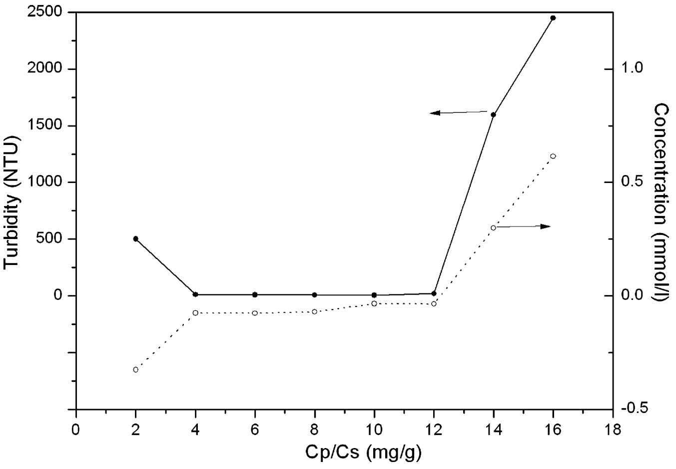


Fig. 4. Residual turbidity (closed symbols) and charge (open symbols) of the supernatant as a function of polymer per substrate (Cp/Cs, mg/g) in Blauton flocculation with CH2.

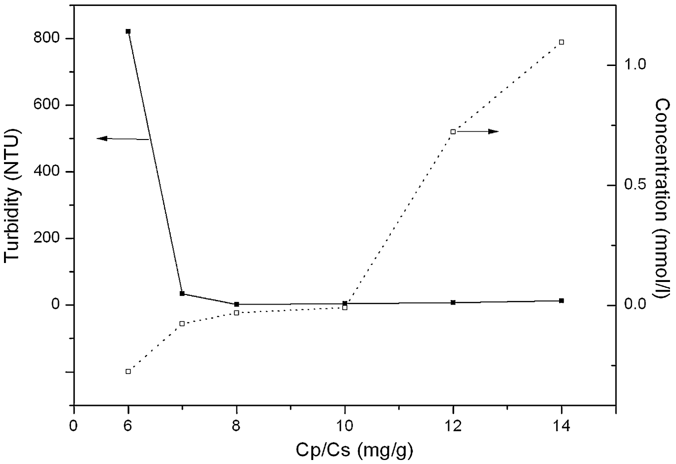


Fig. 5. Residual turbidity and charge of the supernatant as a function of polymer per substrate (Cp/Cs, mg/g) in Blauton flocculation with PA.

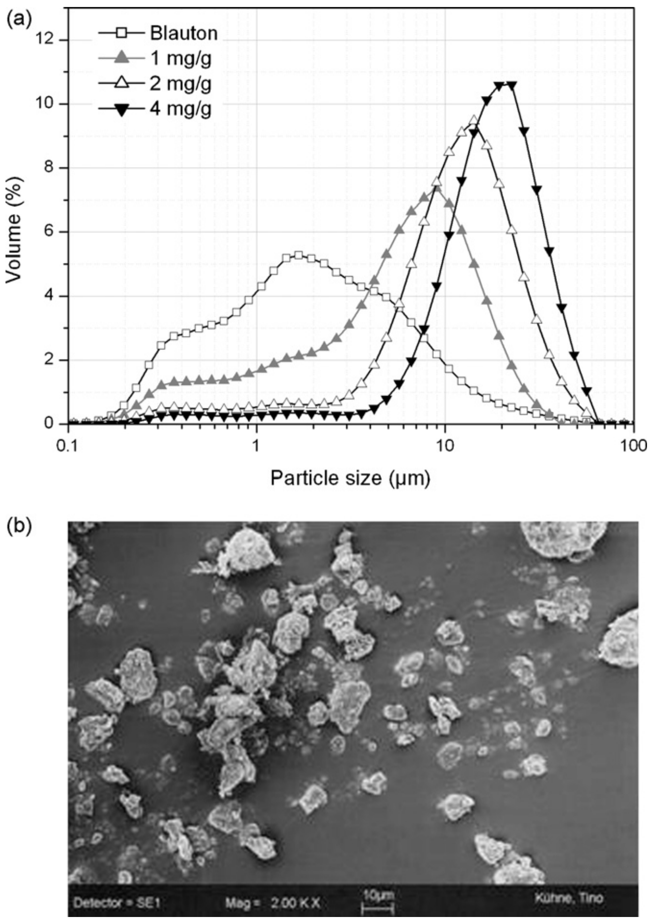


Fig. 6. (a) Particle size distributions of the untreated Blauton and of flocculated Blauton using various PolyDADMAC concentrations and (b) SEM image of Blauton.

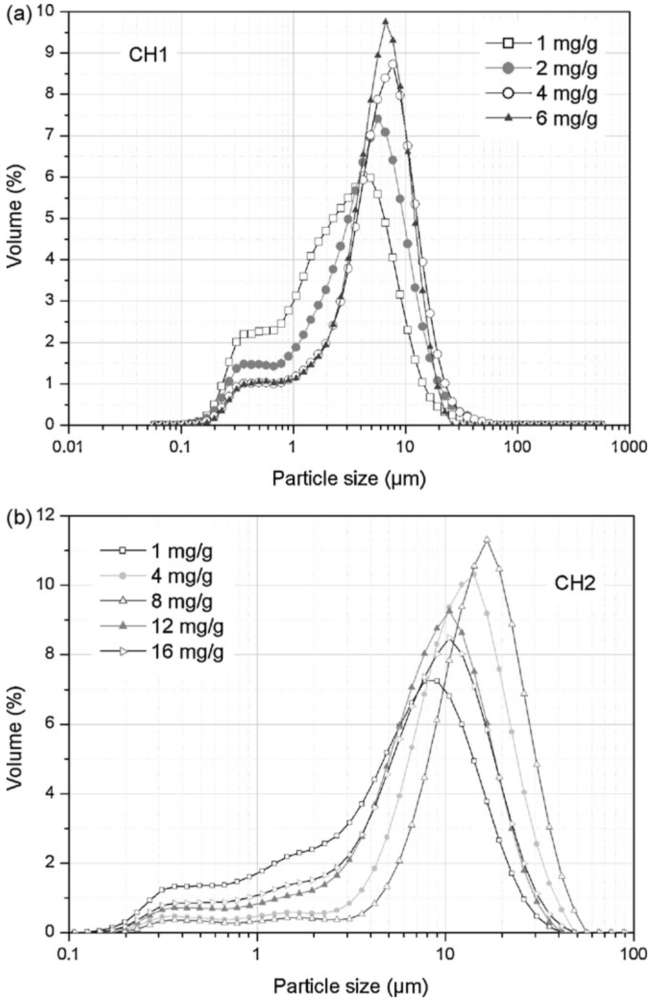


Fig. 7. Floc size distribution of Blauton dispersions using various concentrations of (a) CH1 and (b) CH2.

sample flocculated with PA, not only the supernatant is positively charged at much lower concentrations but also no restabilization occurs even when relatively high polymer concentrations are used. These observations verify the hypothesis that this low charge density polyelectrolyte follows the bridging flocculation mechanism. In this case the low charge density and the high molecular weight of the polymer allow the use of the vast majority of the positive charges for the neutralization of the Blauton's negative charges; thus even a small excess of polymer is witnessed as an increase of the positive charge of the supernatant and also no restabilization occurs, since the excess of positively charges chains does not participate in the flocculation.

The particle size distribution and the SEM image of Blauton show in good agreement an average particle size of 2 μm in dispersions at pH 6 (Fig. 6a and b). Increasing the amount of the polymer used for the flocculation of Blauton leads to increased floc size (Figs. 6a and 7). At low concentrations (1 mg/g) of PolyDADMAC a substantial number of particles demonstrating a size distribution profile similar to that of Blauton is present. At this polymer concentration the particles are either still charged or neutralized, nevertheless not aggregated. The average particle size is rather low leading, as shown above in Fig. 3, to high turbidity due to poor sedimentation. At higher polymer dosages the low sized population is rather limited and the large flocs become the dominant feature of the size distribution profile. The largest floc size (20 μm) was obtained in the flocculation optimum with clear supernatant at a polymer dosage 4 mg/g. As shown in Fig. 7 the largest floc size for the polymers CH1 and CH2 is encountered at the concentration where the lowest turbidity values were encountered. The floc size measurements were conducted while mixing, reducing probably the number of large flocs, which are more prone to rapture. This could explain the rather small floc size – in comparison to the Blauton particle size – that was observed. In any case, since the same conditions were applied to all samples, the validity of the conclusions derived from the floc size is not in stake, as it was also proved by their complete agreement to the turbidity measurements. The floc size of CH1 at the flocculation optimum is 7 μm. On the other hand, CH2 demonstrated a higher floc size of 18 μm when 8 mg/g of polymer were used. In the case of PA the floc size was rather large, in agreement to previous work (Petzold et al., 2004), out of scale for the laser diffraction measurement to be performed (>550 μm).

4. Conclusion

In this study, we compared the flocculation efficiency of a modified chitosan (CH2) to commonly used commercial polyelectrolytes (CH1, PA and PolyDADMAC). The main advantage of the modified chitosan that was investigated, is its solubility in water due to its positive charge, regardless the pH value that also enhances its effectiveness as a flocculant. Furthermore, CH2 shows comparable efficiency in particle sedimentation to the other cationic polymers used. In addition, its flocculation window was broader than the one demonstrated by the commercial chitosan. Among the polyelectrolytes used, PA, following the bridging flocculation mechanism, has produced the largest flocs (>550 μm). Nevertheless, CH2 demonstrates relatively high floc size, comparable to that of PolyDADMAC and considerably higher than that of commercial CH1. Growing demand for environmentally friendly technologies as well as renewable resources has increased the interest on natural flocculants. A compromise between cost, efficiency, and safety in polyelectrolyte applications needs to be found. We have shown that the modified derivatives of the aminopolysaccharide chitosan can be among the most promising candidates as a replacement of the synthetic flocculants in various industrial sectors.

Acknowledgments

The research project (AiF-Nr. 15066BR) has been supported with budgetary funds of the 'Bundesministerium für Wirtschaft und Arbeit' (BMWA) through the 'Arbeitsgemeinschaft industrieller Forschungsvereinigungen "Otto von Guericke" e.V.' (AiF).

The authors are grateful to Mrs. Marina Oelmann for the performance of the electrophoresis experiments.

References

Ashmore, M., Hearn, J., & Karpowicz, F. (2001). Flocculation of latex particles of varying surface charge densities by chitosans. *Langmuir*, *17*, 1069–1073.

Bolto, B., & Gregory, J. (2007). Organic polyelectrolytes in water treatment. *Water Research*, *41*(11), 2301–2324.

Bratby, J. (1980). *Coagulation and flocculation*. Croydon, UK: Uplands Press Ltd.

Bratskaya, S., Schwarz, S., Laube, J., Liebert, T., Heinze, T., Krentz, O., et al. (2005). Effect of polyelectrolyte structural features on flocculation behavior: Cationic polysaccharides vs. synthetic polycations. *Macromolecular Materials and Engineering*, *290*, 778–785.

Bratskaya, S., Schwarz, S., Liebert, T., & Heinze, T. (2005). Starch derivatives of high degree of functionalization 10. Flocculation of kaolin dispersions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *254*, 75–80.

Bratskaya, S., Avramenko, V., Schwarz, S., & Philippova, I. (2006). Enhanced flocculation of oil-in-water emulsions by hydrophobically modified chitosan derivatives. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *275*, 168–176.

Dautzenberg, H., Jaeger, W., Kötz, J., Phillip, B., Seidel, C., & Stscherbina, D. (1994). *Polyelectrolytes: Formation, characterization and application*. München, Germany: Hanser Gardner.

Dragan, S., Maftuleac, A., Dranca, I., Ghimici, L., & Lupascu, T. (2002). Flocculation of montmorillonite by some hydrophobically modified polycations containing quaternary ammonium salt groups in the backbone. *Journal of Applied Polymer Science*, *84*, 871–876.

Gregory, J. (1987). The stability of solid–liquid dispersions in the presence of polymers. In T. F. Tadros (Ed.), *Solid/liquid dispersions* (pp. 163–181). London, UK: Academic Press.

Petzold, G., Mende, M., Lunkwitz, K., Schwarz, S., & Buchhammer, H. (2003). Higher efficiency in the flocculation of clay suspensions by using combinations of oppositely charged polyelectrolytes. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *218*, 47–57.

Petzold, G., Geissler, U., Smolka, N., & Schwarz, S. (2004). Influence of humic acid on the flocculation of clay. *Journal of Colloid and Polymer Science*, *282*, 670–676.

Renault, F., Sancey, B., Badot, P. M., & Crini, G. (2009). Chitosan for coagulation/flocculation processes—An eco-friendly approach. *European Polymer Journal*, *45*, 1337–1348.

Rose, G. R., & St. John, M. R. (1987). Flocculation. In J. I. Kroschwitz (Ed.), *Encyclopedia of polymer science and engineering* (pp. 211–233). New York, USA: John Wiley and Sons.

Roussy, J., Van Vooren, M., & Guibal, E. (2005). Influence of chitosan characteristics on coagulation and flocculation of organic suspensions. *Journal of Applied Polymer Science*, *98*, 2070–2079.

Tripathy, T., & Rajan De, B. (2006). Flocculation: A new way to treat waste water. *Journal of Physical Sciences*, *10*, 93–127.

Zeng, D., Wu, J., & Kennedy, J. F. (2008). Application of a chitosan flocculant to water treatment. *Carbohydrate Polymers*, *71*, 135–139.