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New cationic polyelectrolytes for flocculation processes of baker's yeast waste water

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Summary

New cationic polyelectrolytes synthesized by homopolymerization or copolymerization of allyl-acrylate quaternary ammonium salts with acrylamide (AAm) and diallyldimethylammonium chloride (DADMAC) were tested as flocculants in a baker's yeast waste water. The effect of polymer structure, molecular weight and charge density on the flocculation properties were investigated with respect to total organic content, optical density and volume of sludge. The results were compared with that of a commercial polyelectrolyte Zetag 7557 (acryloxyethyltrimethylammoniumchloride-acrylamide copolymer) (Allied Colloids). The flocculation results indicated that the efficiency of the new copolymers was similar to commercial polyelectrolyte Zetag 7557 and both polymer bridging and charge patch models are effective.

Introduction

Synthetic polyelectrolytes are polymers of major significance due to their increasing application areas. They are used as flocculants, coagulants or dewatering agents in processes of water purification and waste water treatment, as stabilizers in emulsion polymerization, in paper making, food, cosmetics and pharmaceuticals [1-4]. Polyelectrolytes with opposite charge are used for flocculating clay, silica, or cellulose [5-9]. Due to electrostatic bonding and polymer bridging these polymers produce large flocs and cause settling. Polyelectrolytes with high charge density and high molar masses cause aggregation according to the so called charge patch model [8]. Adsorption of polyelectrolytes minimizes repulsion between particles, and the surfaces with opposite charges aggregate due to Coulomb forces. Linear polyelectrolytes with low charge densities and high molar masses form bridges between colloidal particles and cause aggregation according to the so called bridging model. Cationic polyelectrolytes (generally quaternary ammonium salts) with various charge densities have been synthesized either by copolymerization of charged and uncharged monomers or modification of known polymers [10-16]. The copolymers of acrylamide (AAm) with cationic charged comonomers have been the most common polymers for flocculation [14-16]. Also flocculants based on cationic starches were used to enhance biological degradability of polymers. Dewatering efficiencies were found to be comparable with those of synthetic polymers at higher concentrations [17].

In our previous works, a series of allyl-acrylate quaternary ammonium monomers were synthesized, homopolymerized and copolymerized with AAm and DADMAC to obtain moderate molecular weight polymers with various charge densities [18-20]. The aim of this work is to study the effect of structure, charge density and molecular size of these polymers on the flocculation process in comparison with a commercial polyelectrolyte, copolymer of acryloyloxyethyltrimethylammonium chloride and acrylamide (Zetag).

Experimental

Materials

The cationic polyelectrolytes have been synthesized by copolymerization of acrylamide and DADMAC with allyl-acrylate quaternary ammonium salts. The synthesis of allyl-acrylate quaternary ammonium salts and their copolymers with DADMAC and AAm have been reported elsewhere [18,19,20]. The structures of the monomers are given in Figure 1. The representative procedure for the synthesis of one of the acrylamide-allyl-acrylate quaternary ammonium salt copolymers is given below.

Copolymerization of acrylamide with allyl-acrylate quaternary ammonium salts

The copolymerizations were carried out in 25 –mL, septum-sealed glass tubes. For the synthesis of copolymer **2a** [N,N-piperidyl-N-2-(ethoxycarbonyl)allyl allyl ammonium chloride]–AAm (33:67 mol %), **2a** (0.96 g, 0.0035 m) and AAm (0.497 g, 0.007 m) were dissolved in 5 mL of water. 2,2'-azo-bis(2-amidinopropane) dihydrochloride (V-50) (0.00135 g) was added, and the tubes were subjected to four freeze-evacuate-thaw procedures. The tubes were then placed in a 52-54 ^{0}C oil bath. The copolymers were precipitated into ethanol or acetone and dried under vacuum. The yields for **2a**-AAm and **2b**-AAm copolymers were 50.0 and 14.0 % after precipitation.

The yields for DADMAC, **1a**, **3a**-DADMAC and **3b**-DADMAC polymers were 63.0, 90.5, 55.5 and 65.0 % after precipitation and 7.4, 18.8, 21.0 and 17.0 % after dialysis aginst water using tubing with a molecular cutoff of 6000-8000 [19].

Copolymer compositions of DADMAC copolymers were found using the integrated ^{13}C-NMR spectroscopy. Because the solutions AAm copolymers were highly viscous at very low concentrations ^{13}C-NMR could not be used for the estimation of copolymer compositions. Therefore copolymer compositions of acrylamide copolymers were obtained by colloidal titration using 0.000115 M potassium poly(vinyl sulfate) (PVSK) solution as the titrant and toluidine blue as indicator [21].

In this study, biological sludge of a baker's yeast factory was used for flocculation experiments. Table 1 shows the characteristics of waste water samples. Inorganic carbon (IC) of the samples were measured using Ionics 155 carbon analyzer. Jar test flocculation procedure using a 6 paddle stirrer (Velp Scientifica, FC4S) was used. The sample volume was 1000 ml, polyelectrolyte concentration was 15 mg/L, agitation rates were 200 rpm for 5 min. Settling period was 5 min, and the samples of supernatant were taken. The degree of clarification was determined by optical-density (OD) measurements with a Shimadzu 1240 UV-Visible Spectrophotometer at a wavelength of 600 nm. The total organic content (TOC) values of the supernatant and volume of sludge were determined.

Table 1. Characterization of wastewater

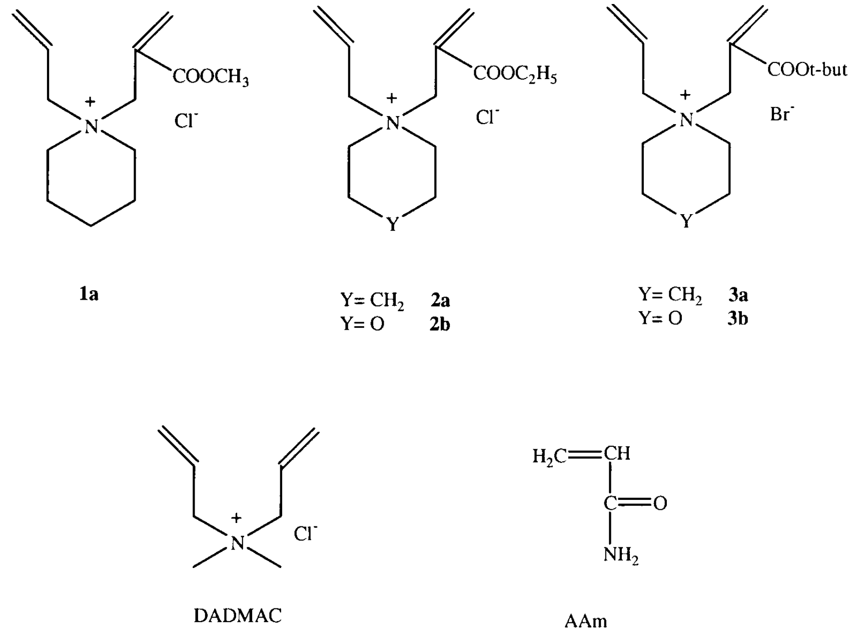
Parameters	Value
pH	7.5
Solid content (g/L)	19
Volatile material (g/L)	11.99
TOC (mg/L)	6050
Total carbon (TC) (mg/L	6600
Inorganic carbon (IC) (mg/	550

Result and Discussion

The polyelectrolytes used in this study can be divided into two groups: pDADMAC type and polyacrylamide type polymers. PDADMAC type polymers were homopolymers of DADMAC and N,N-piperidyl-N-2-(methoxycarbonyl)allyl allyl ammonium chloride (**1a**), and copolymers of N,N-piperidyl-N-2-(t-butoxycarbonyl)allyl allyl ammonium bromide (**3a**) and N,N-morpholine-N-2-(t-butoxycarbonyl)allyl allyl ammonium bromide (**3b**) with DADMAC (Figure 1). The polymers were synthesized in water at 60 ^{0}C using V-50 as the initiator [19]. The total monomer and initiator concentrations were 3 M and $0.5\text{x}10^{-2}$ M, respectively. The characteristics of the polymers are given in Table 2. The allyl-acrylate monomer amounts in the copolymers were 30 mol % for **3a**-DADMAC copolymer and 24 mol % for **3b**-DADMAC copolymer. Polyacrylamide type polymers were the copolymers of AAm with **2a** (N,N-piperidyl-N-2-(ethoxycarbonyl)allyl allyl ammonium chloride) and **2b** (N,N-morpholine-N-2-(ethoxycarbonyl)allyl allyl ammonium chloride) (Figure 1). Since AAm is more reactive than DADMAC copolymerization of allyl-acrylate monomers with AAm under the same conditions were too fast to control, giving polymers during freeze-evacuate-thaw procedure. Therefore the total monomer and initiator concentrations were lowered to 2 M and $1\text{x}10^{-3}$ M and polymerizations were done at 52-54 ^{0}C. The allyl-acrylate units in **2a**-AAm and **2b**-AAm copolymers were 28 and 31 % as determined by titration with PVSK solution [20]. The ^{1}H-NMR spectrum of the copolymers showed no double bonds, indicating complete cyclization of allyl-acrylate monomers to give linear polymers with pyrrolidinium rings at the backbone.

It is known that aqueous solution properties of polyelectrolytes are strongly affected by salts which causes reduction of the polymer chain and thus reducing flocculation properties. The polymers with zwitterionic groups (contain both positive and negative charges) expand with increasing salinity. Therefore the ester groups of **3a**-DADMAC copolymer were hydrolized completely in trifluoroacetic acid to give a polymer with both cationic and zwitterionic groups.

All pDADMAC type polymers had high charge densities (100 %) due to cationic groups in every repeat unit of the polymer whereas charge densities of AAm type polymers were lower because the ionic (**2a** and **2b)** contents were about 30 mol %,



1a

DADMAC

AAm

Figure 1. Structures of the monomers

only. Intrinsic viscosity is a measure of the hydrodynamic size of the polymer molecule in solution. An increase in hydrodynamic volume will enhance the flocculation due to an increase in bridging. Intrinsic viscosities of two homopolymers (pDADMAC and poly-**1a**) were similar around 2.0. The intrinsic viscosities of the copolymers except **2b**-AAm copolymer were around 3.0. The highest viscosity copolymer (**2b**-AAm copolymer) (7.1) was used to evaluate the effect of the molecular size on the flocculation efficiency of the polymer.

Table 2. Polymer composition and intrinsic viscosities of the new polymers

Monomers	Polymer Compositio	Intrinsic viscos
DADMAC	-	1.99
1a	100	2.02
3a-DADMAC	30:70	3.10
3b-DADMAC	24:76	3.20
3a-DADMAC (hydrol.)	30:70	3.10
2a-AAm	28:72	3.00
2b-AAm	31:69	7.10

[a] Intrinsic viscosities were measured in 0.09 M NaCl at 36+/-0.2 ^{0}C

For the sludge dewatering applications it was reported that both high charge density and high molecular weight are required. Although charge densities and molecular weights of the polymers were different, sludge dewatering curves for all tested polymers had similar shapes (Figure 2). The efficiency increased with the increase of the polyelectrolyte concentration. A plateau was observed after the polymer concentration of 15 mg/L. At a 15 mg/L polymer concentration settling time ranged between 10 and 13 sec. Figure 3 shows comparative results of sludge volumes obtained using 15 mg/L of the polyelectrolytes tested. Sludge volumes were about 64-77 % of control samples. The sludge volume of copolymer **3a**-DADMAC hydrolized was highest (77% of the control), confirm the less efficient flocculation property of this copolymer. This behavior is due to the lowest charge density of this polymer among the polymers tested. Sludge volume of Zetag 7557 was found to be 69 % of control sample.

Figure 4 shows the optical densities of residual solutions after 5 minutes of settling times at the jar test flocculation experiment using a polymer dose of 15 mg/L. The copolymers **3a**-DADMAC and **3b**-DADMAC with similar structures, charge densities (100 %) and molecular sizes (intrinsic viscosities= 3.1-3.2) were the most efficient among the synthesized polymers. The effect of molecular size can be observed by comparison of flocculation efficiencies of polymers **2a**-AAm and **2b**-AAm. Increase of flocculation efficiency of the polymer **2b**-AAm with increasing viscosity is associated with the bridging flocculation mechanism. The homopolymer **1a** was found to be more efficient than the homopolymer of DADMAC, indicating the more effective structure of allyl-acrylate monomers compared to DADMAC. The pDADMAC type polymers were more efficient than pAAm type polymers indicating that the charge-patch flocculation mechanism is more effective than bridging flocculation mechanism. The low efficiency of **3a**-DADMAC hydrolized polymer was probably due to a decrease in charge density. Optical densities of the synthesized polymers were 25-68 % of the control sample. Zetag 7557 was found to be the most efficient among the tested polymers.

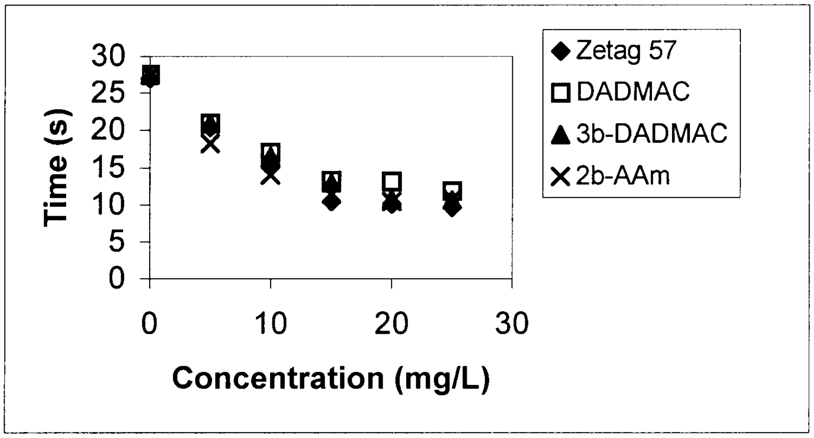


Figure 2. Sludge dewatering curves

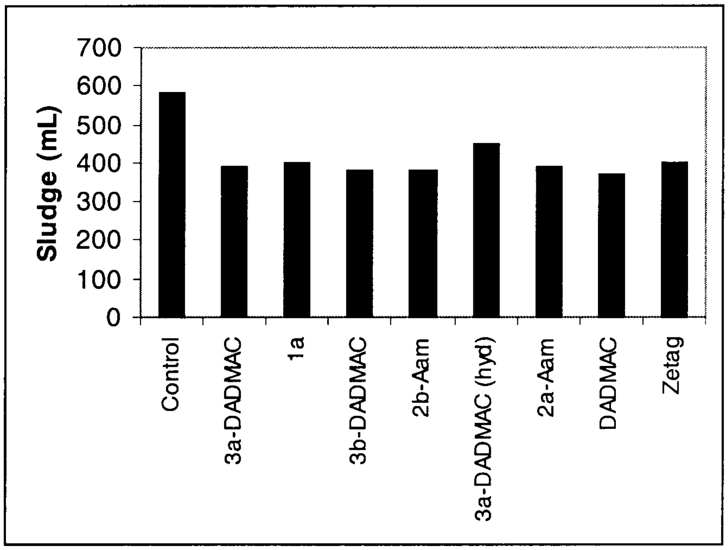


Figure 3. Sludge volumes obtained with the polyelectrolytes tested

TOC efficiencies for the polymers were compared, using the same dosage of polymers (15 mg/L). TOC values observed for most polyelectrolytes (pDADMAC, **3a**-DADMAC, **3b**-DADMAC, **2a**-AAm, **2b**-AAm) were similar, around 50 mg/L. This value was 62 % of the value of the control sample (80mg/L). TOC values for polymers **1a** and **3a**-DADMAC(hydrolized) were highest (60 mg/L) among the polymers tested. The TOC value obtained for Zetag 7557 was 66 % of the control value. As a result the efficiencies of most of the synthesized polymers were similar to the commercial polymer.

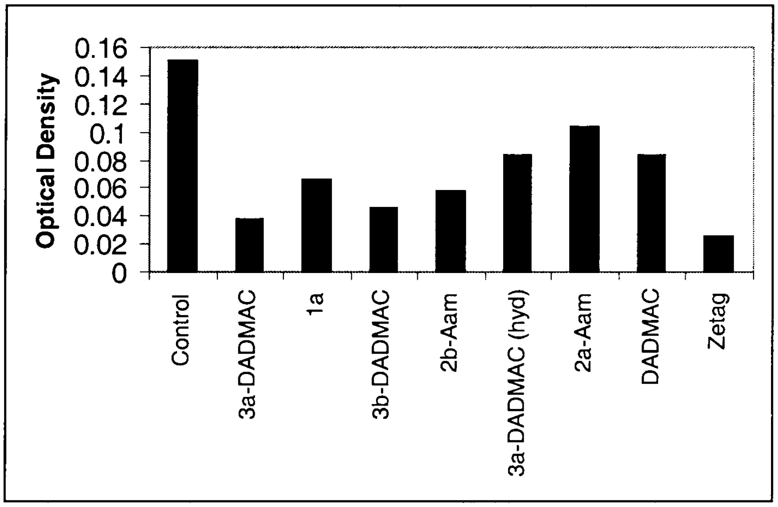


Figure 4. Optical densities obtained with the synthesized polymers

In conclusion, by copolymerizing acrylamide or DADMAC with allyl-acrylate monomers it is possible to produce polymers with different charge densities, molecular weight and chemical structures. The efficiency of the polyelectrolytes tested can be increased by increasing charge densities of AAm copolymers and by increasing the molecular weight of DADMAC copolymers.

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