HUNGARIAN JOURNAL
OF INDUSTRIAL CHEMISTRY
VESZPRÉM
Vol. 31. pp. 3-8 (2003)

CHEMICAL UTILIZATION OF BIOMASS I: STARCH MODIFICATION IN BATCH TYPE SOLID PHASE REACTOR

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Anionic flocculants were produced by chemical modification of starch. On the basis of their favourable properties (non-toxic, environmentally degradable) their application is very advantageous in drinking water treatment, food industry and pharmaceutical industry for removing colloid size particles from suspensions. The Greenfloc 213A flocculant developed at the Department of Chemical Engineering Science of the University of Veszprém was successful both in laboratory and industrial scale experiments. A pilot scale plant was built for the production of the flocculant. The main part of the plant is a multifunctional batch type reactor in which all steps of the dry modification technology can be carried out. The scaling-up of the reactors requires thorough knowledge of the kinetics of the reactions taking place in the equipment. The starch modification reaction consists of the phosphorylation and degradation of the starch. The results of the kinetic investigation and the bath type pilot scale plant will be presented in this paper.

Introduction

Flocculants are so called polyelectrolytes, water-soluble polymers with ionic charge. The particles in aqueous suspension can be agglomerated by various mechanisms. Flocculants neutralise the identical charges of repelling particles and hence stop repulsion. Another mechanism is bridge forming, where the big polymer molecule binds particles to itself by its functional groups. Cationic flocculants are suitable for the neutralisation of particles with a negative charge, while anionic ones are for those with a positive charge.

The flocculants used in today's industry are mostly synthetic products, such as polyacrylamid, polyethylene-oxide, etc. These are very effective, but may contain toxic monomer residuals and after disposed of in the environment they are not biodegradable.

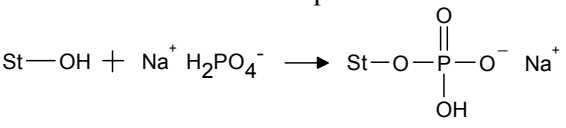
Starch in its original form is not water-soluble and has no functional groups with charges. It is a mixture of two polymers: amylose and amylopectin, and the mass of molecules ranges from 50,000 to millions.

Starch can be converted into flocculants by substituting some of the OH^--groups in the monomer units of the polymer chain with ionic functional groups. As a result of the substitution the water-solubility of the starch derivative increases. Depending on whether we build anionic or cationic functional groups into the starch chain, we will get anionic or cationic flocculants.

The starch derivative if produced with the proper reagent is non-toxic and indeed biodegradable.

The objective then is to produce natural based flocculants for those fields where their beneficial properties are really advantageous. Such a field is drinking water treatment, where in the clarification step anionic flocculants are used. Al^{3+} or Fe^{3+}-salts are added to the water to be treated, and polyelectrolytes improve the sedimentation of the forming flocs.

By building phosphate groups into the starch anionic derivatives can be produced:



The building-in of phosphate groups can be made more effective by the use of N-containing catalysators.

Lab-scale experiments for the development of the starch based anionic flocculant

At the Department of Chemical Engineering Science of the University of Veszprém a research group has been involved in chemical processing of the ingredients of plant biomass for a long time. The aim of the work is to produce chemicals based on renewable raw materials, which can substitute the commercial products synthesized from fossil raw materials.

The laboratory experiments related to the development of starch based flocculants were of two kinds, preparation of polyelectrolytes and testing of the best products in different applications.

The starting materials of the modification procedures were native corn starch, wheat starch and waxy corn starch. Phosphoric acid and phosphate salts were used to build the phosphate groups into the starch molecule, and different kind of N-compounds were used to catalyse the phosphorylation reactions.

Wet (slurry phase) and dry (solid phase) reactions were carried out. The reaction parameters (temperature, concentration, etc.) were chosen so that we could prepare polyelectrolyte with solubility as high as possible, satisfactory ionic character and high molecular weight.

The best flocculant was a starch phosphate with an average molecular weight of $M_w \approx 1.8*10^6$ Da, and a degree of substitution DS≈0.01. The phosphorylation reaction was carried out in solid phase. The product was registered by the name of Greenfloc 213A.

We recommend Greenfloc 213A to use it as a coagulant aid in the drinking water treatment together with Al- or Fe-salt coagulants.

Industrial scale application tests [1]:

The experiments related to the applicability of the Greenfloc 213A were conducted in Lazberc at the North-Hungarian Waterworks Ltd. In this area the environmental protection is especially important: Lazberc is in the heart of the Bukk Mountains – a natural park.

The objective of the experiments in the waterworks was to find out whether the flocculant developed by us is suitable for the substitution of the synthetic agent in the coagulation-flocculation step of water treatment. At these waterworks coagulation was followed by sedimentation.

From the characteristics (turbidity and COD removal, Al-residue and algae removal) this time the algae removal has been followed with special attention. The sedimentation is made difficult not only by the high number of algae, but by the variety of algae types. With the coming winter this is accompanied by the increasing viscosity of water.

Table I: Results of the experiment in Lazberc (1 November - 31 December 2003)*

Property	Removal percent after sedimentation		
	1-16 Nov. by synthetic flocculant	17 Nov.-8 Dec. by Greenfloc 213A	9-31 Dec. by synthetic flocculant
Turbidity, NTU	89.6	87.5	84.0
COD, mg/L	43.8	43.2	32.4
Algae, 10^6/L	92.8	93.6	92.0
Al(III), mg/L	99.96	99.96	99.94
Temperature, ^oC	6-7	4-6	3-4

*Coagulant: BOPAC (poly-aluminium-chloride)

The figures in Table I. and in charts in *Fig. 1*. show that the characteristics of the water produced using Greenfloc 213A are similar to those that were measured before and after the experiment.

After the successful industrial scale experiments we decided to build a pilot scale plant for the production of the starch based flocculants. The scaling up of a reactor requires special attention since because of the larger quantities the manipulation times are longer in the larger pilot scale reactor than in the laboratory reactor. That is why we have to investigate thoroughly the kinetics of the phosphorylation process.

Kinetics of the modification

During the chemical reaction the building-in of phosphate groups and the degradation of polymer molecules take place simultaneously. However flocculants have to be of high molecular weight for bridge-forming. Therefore the temperature and time of the reaction have to be optimised. The optimal reaction conditions were defined by parallel investigation of the two chemical reactions and flocculation properties.

The phosphorylation reaction was carried out at different temperatures, and the quality of the products was followed by determining the bound and free phosphorus in the starch phosphate. At the same time the degradation reaction was examined through the analysis of the molecular weight

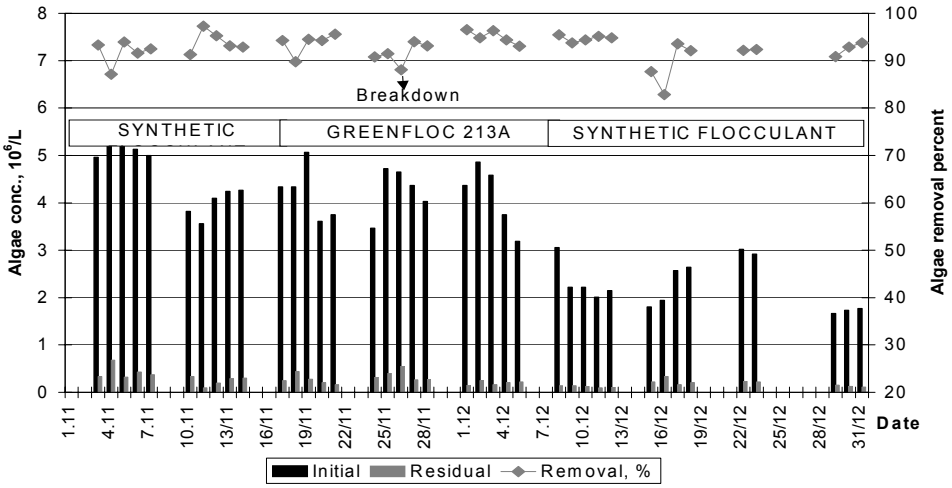


Figure 1: Algae removal in the Lazberc water treatment plant

distribution of the derivatives. The flocculation properties were tested by settling standard kaolin suspension.

Materials and methods

The raw material Meritena 300 starch was supplied by Hungrana (Hungary), all of the other ingredients used at the phosphorylation were of analytical grade. The chemicals used at the analysis were bought from Merck AG in analytical reagent grade.

Analysis of the bound and free phosphorus-content: The free phosphate content of the samples was separated from the bound phosphate by extraction with 80% aqueous methanol. All organic materials of the solid residue were burnt, and the P-content was determined from the ash as molybdivanado-phosphoric acid spectrophotometrically [2] by Biochrom 4060 spectrophotometer (Pharmacia AG) at 460 nm. The liquid phase was evaporated and the free P-content was determined from its residue in a similar way.

Determination of the molecular weight distribution: In the standard method the starch phosphate samples were dissolved in 90% aqueous dimethyl-sulfoxid solution for 24 hours. (The native starch samples were dissolved for 94 hours.) The molecular weight distribution was measured by HPSEC analysis: Gilson HPLC system, 30 cm × 7,8 mm ×10 µm TSK-GEL G5000PW$_{XL}$ column, 20 µL sample injected, 0.6 mL/min pH 11 puffer eluent [3], 60 ^{o}C thermostat, RID detector. The parameters of the molecular weight distribution were determined by a Microsoft Excel program.

Flocculation characteristics: The flocculation properties of the derivatives were measured by a quick test developed at our department. 10 mL of kaolin suspension (5 g/L) was filled into test-tubes and 0.1-0.5 mL of flocculant solution (1 g/L) was added and the mixture was thoroughly mixed. Some seconds after the stoppage flocs appeared and settled into the lower part of the tubes. The time of the appearance of the flocs and the time of their settling were measured. The flocculation characteristics of the flocculants in a particular application were determined by jar tests and followed common water analytical methods.

Results and discussion

As a result of the preliminary laboratory experiments we had a receipt and a method for

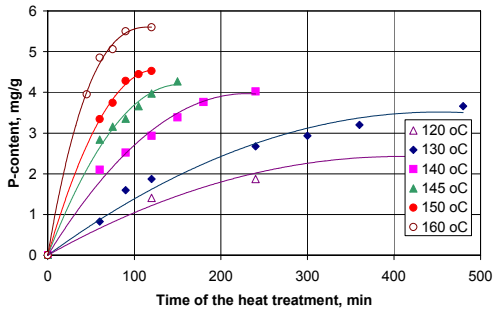


Figure 2: Bound P in the modified starch

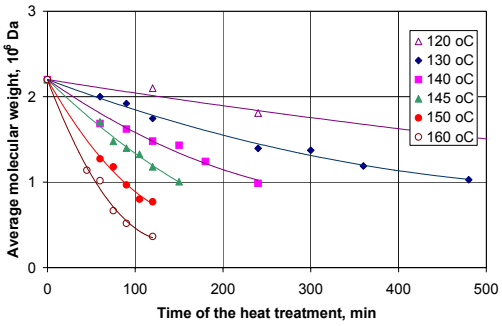


Figure 3: Molecular weight decrease during the heat treatment

preparation of the Greenfloc 213A flocculant. The objective of this kinetic investigation was to clear up the influence of the longer residence time and possibly irregular temperature on the quality of the product.

The raw material starch was impregnated with the additives according to the receipt, and the wet material was treated at temperatures 120-160 °C. The duration of the heat treatments ranged 45-1440 minutes depending on the temperature. The reaction products were analysed and tested. All product samples could be dissolved by the standard HPSEC method.

Fig. 2 shows the building-in of the phosphorus into the starch during the time at different temperatures. In Fig. 3 the degradation of the starch polymers is displayed by an average molecular weight versus time diagram.

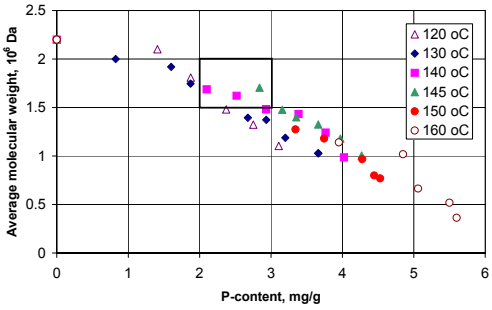


Figure 4: Molecular weight vs. P-content diagram

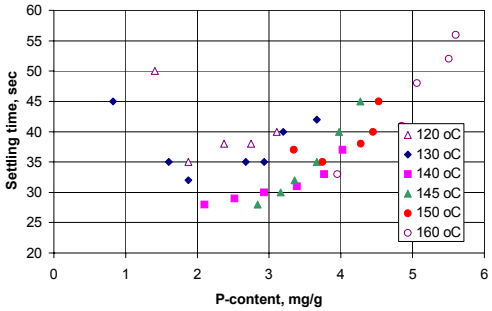


Figure 5: Flocculation properties of the products

Based on these data we can draw an average molecular weight versus bound P-content diagram (Fig. 4.), in which a limited area contains the characteristics of the products resulted from the given raw material composition. In the diagram we can determine the range where the "best products" can be found. Fig. 5 shows the results of the flocculation test at 20 ppm dosage. Applying the best flocculants the kaolin suspension settled in under 30 sec. The average molecular weights of these derivatives range from $1.5\text{-}2*10^6$ Da, the P-content is 2-3 mg/g. The products of $1\text{-}1.5*10^6$ Da molecular weight and 3-4 mg/g P-content showed rather good flocculation effect, but the flocs were smaller.

In this way we can state that

- the best flocculant can be prepared at 140 °C and 90 min;
- the time of the heating up from the drying to the reaction temperature must be short;
- the conversion under the heating up can be determined from the results.

Pilot scale reactor

We have developed and constructed a pilot scale batch type reactor of 100 kg/charge (Fig. 6), which is suitable for performing solid phase reactions especially when the main component is a fine grain solid material (generally lower than 200 μm). The shape of reactor is a horizontal cylinder closed at both ends. Its diameter is D=0.9 m, length is L=0.9 m, and volume is V=0,45 m^3. The adequate motion of the particles is ensured by an impeller. The rotation speed of the impeller can be set in an 8-90 rpm range depending on technological aims. The even distribution of the dissolved reagents on the surface of particles of the main component is carried out by a pneumatic nozzle. In the course of spraying the agglomeration of particles also takes place. Over-agglomeration is prevented by a high rotation speed chopper (2440 rpm) placed at the bottom of the reactor.

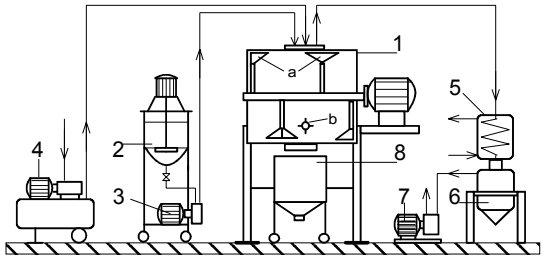


Figure 6: Flow sheet of the pilot scale plant
1 - reactor, a-impeller, b-chopper; 2 - liquid tank; 3 -liqiud pump; 4 - compressor; 5 - condenser; 6 - container for condensed vapour; 7 - vacuum pump; 8 - container for product

The reactor is equipped with proper insulation and an electric heating jacket to ensure the heat energy input required for the reaction. The maximum temperature is 180 ^{o}C. A liquid tank belongs to the reactor with a heating jacket to dissolve reagents and a compressor to provide compressed air for spraying. The vapour formed during the heat treatment (drying, heating, chemical reaction) is eliminated by a vacuum pump and then it is condensed.

Production of modified starch in the pilot scale reactor

The chemical reaction is performed in the solid phase. Apart from the starch all other components are water-soluble; therefore we add their aqueous solution to the starch before the reaction.

The steps to be carried out in the reactor are the following:

- Spraying in the aqueous solution of the reagents and mixing it with the starch;
- Drying the impregnated starch;
- Heating up to the optimal reaction temperature;
- Performing the phosphorylation reaction.

At the first step it is very important to add as little water as possible into the reactor to keep the flowability of the particles during the operation as well as to reduce the energy demand of drying.
The temperature of drying and hence the speed of drying is restricted by the fact, that starch, in presence of water, gelatinises at a higher temperature. (Native starch at ca. 70 ^{o}C, modified could differ.) Gelatinised starch is impossible to handle in such an apparatus.

During the experimental production of Greenfloc 213A we have measured anionic flocculant and controlled the temperature of the reactor wall as well as the temperature inside the reactor. During the drying period the wall temperature was set to 80 ^{o}C, and no significant gelatinisation was experienced. The remaining (3-5 m%) humidity was eliminated in the heating-up phase at a wall temperature of 120 ^{o}C. The phosphorylation reaction was performed at a wall temperature of 140 ^{o}C.

Properties of the Greenfloc 213A flocculant

Fig. 7 shows the size exclusion (HPSEC) chromatograms of the native starch and the Greenfloc 213A anionic flocculant derived from it. At first the native starch was dissolved according to the standard method described above. The area beneath the curve is proportional to the amount of material that can be dissolved. Only a small part of the native starch – mainly the polymers of lower molecular weight – could dissolve in this way. The diagrams show that the solubility of the polymers of higher molecular weight was increased by the phosphorylation. The chromatogram of the native starch after a more intensive dissolution is also displayed in Fig. 7. During the modification reaction the rate of the polymers of lower molecular weight is increased, but the degradation is not significant.

The main characteristics of the Greenfloc 213A produced in the pilot scale plant are:

- Average molecular weight (M_w) – 1.74*10^6 Da
- Bounded P-content – 2.74 mg/g
- Settling time at 20 ppm – 26 sec
  10 ppm – 28 sec.

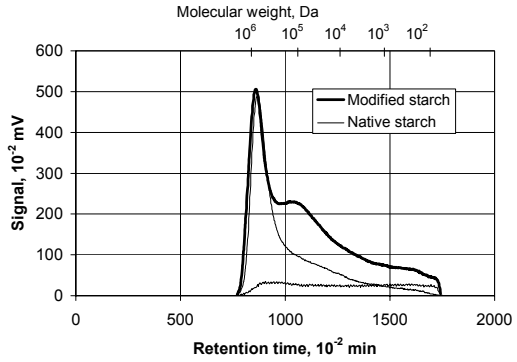


Figure 7: Size exclusion chromatograms of the modified starch (Greenfloc 213A) and the native starch after standard and intensive dissolution

Conclusions

- The flocculant, produced by the reactor had the same characteristics and efficiency as the product made in the laboratory
- The Greenfloc 213A is a really tailor-made product; it has optimal molecular weight and P-content.
- The reactor could be operated without any problem, and all steps of the technology could be carried out according to the expectations.

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