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Green wastewater treatment flocculants and fixatives prepared from cellulose using high-consistency processing and deep eutectic solvents

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ABSTRACT

Cellulose offers a large renewable raw material base and can be chemically modified in a variety of ways to introduce new functionalities such as cationic charge, that are required in effective waste water treatment for any polymers. Cationic cellulose derivatives were synthesized using both conventional and novel methods from several commercially available cellulose pulps. The cationic derivatives were used as biobased flocculants to treat real-life wastewater samples in a head-to-head comparison with cationic polyacrylamides. A novel high-consistency, high shear mixing heterogeneous mixing method enables the preparation of cellulose derivatives without the use of **solvent** or high cost solubilization methods. When higher cationic charge is required, deep eutectic solvents can be used to modify cellulose. Both the molecular weight and charge of the cationic cellulose derivatives have a drastic influence on performance in water treatment applications. Flocculation experiments with real-life waste water samples revealed that cationic cellulose derivatives are able to effectively function as flocculants and fixatives, and even outperform commercial polyacrylamides. The highest achieved level of turbidity removal was 93.2%. Cationic cellulose derivatives provided good efficacy in sludge dewatering, Focused Beam Reflectance Measurement flocculation tests and anionic trash fixing, which are crucial properties for the pulp and paper industry.

1. Introduction

The increasing demand for the use of sustainable materials in industrial applications has created a need to develop technologies that enable the use of biopolymers such as cellulose for the replacement of petroleum-based chemicals. Effective purification of wastewater is one of the most crucial questions of the future that demands a long-term solution. Cellulose is one of the most abundant natural polymers and could be a primary chemical resource in the future due to its renewability, biodegradability, biocompatibility and extensive derivatisation capacity [1]. The strong intra- and intermolecular hydrogen bonds in cellulose create difficulties when cellulose needs to be processed using industrially-applicable methods, and strong chemical or enzymatic modification of cellulose is needed to enforce its compatibility, especially with petroleum-derived components [2]. Cationisation of cellulose has been found to have significant industrial importance from several areas including the paper, cosmetics, textiles, food packaging and water purification industries [3–6]. In the textile industry, cationic cellulose is mainly used to remove acidic dyes from aqueous eluents and thus diminishing environmental stress of these processes [7]. In the paper industry, cellulose fibres are used to improve the mechanical properties of dispersions and composites, to purify process water and to provide specific functionalities for paper products [8]. The use of cationic cellulose to purify waste waters from various sources has also been suggested [8–11]. Cellulose fibres naturally contain O and COO groups resulting from the deprotonation of small amounts of carboxylic acid and alcohol groups, and are thus negatively charged. Cellulose repels anionic dyes as well as anionic filler particles in dispersions unless it is chemically modified, and cationisation is generally used to modify cellulose to enable its use in these applications. Colloids in water are also usually negatively charged, and a high content of cationic groups in the cellulose derivatives is needed to reach high flocculation capacity. Flocculation is an effective and economical way of purifying wastewater. Common industrial–Scale flocculants used for this purpose are polyacrylamides or amines, typically copolymers of acrylamide and sodium acrylate. Cationic polyacrylamides have traditionally been used for these purposes due to their relatively low price [12]. However, with industrial development, the amount of wastewater has increased significantly, and the demand for effective, cheap and environmentally friendly flocculants for the treatment of various kinds of wastewater is becoming increasingly high. Cellulose could provide a long-term solution for this dilemma, if industrially-applicable methods

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can be used for its cationisation. Cationic cellulose has been reportedly to be prepared both using heterogeneous [3,9,13,14] and homogeneous [7,8,10,9–11] reaction methods utilizing various cationisation reagents, yet using glycidyl trimethylammonium chloride (GTAC or EPTMAC) has been the prevalent choice [8–10,13–18]. Such cationisation systems have also been reportedly for cationic xylan [19–23] and well-documented for preparing cationic starch [24–26]. However, high cationic charge has only been acquired using homogeneous modification methods, which have demanded the use of expensive and toxic solvents such as dimethylacetamide that are incapable of competing with the manufacturing price of cationic polyacrylamides. Furthermore, there is only a limited number of reports available on the flocculation performance of such cationic cellulose derivatives with real-life wastewater samples and these have not involved head-to-head comparison with commercial polyacrylamides, which are considered as the golden standard of wastewater treatment [8,27]. The aim of this work was to evaluate different methods to prepare cationic cellulose derivatives and compare their performance properties in different flocculation tests against commercial flocculants. The potential of the cationic cellulose derivatives as flocculants was evaluated using standard industrial flocculation tests with three different types of real-life wastewater samples. The performance of the cationic cellulose derivatives was compared to that of synthetic cationic polymers currently used for this purpose. The influence of the properties of cellulose were also studied, and the suitability of different cellulose pulps were compared for this particular purpose. Part of the discussion and interpretation of the results presented in this paper are based on the raw data originally published in the public Fubio Biorefinery Program report, which has limited availability. In the Future Biorefinery program, cationic cellulose derivatives were prepared using heterogeneous and homogeneous modification methods to compare the different methods, and to study the effect of charge and other polymer properties on the flocculation performance [9]. In addition, cationic cellulose derivatives were synthesized using a novel method based in the use of deep eutectic solvents.

2. Materials and methods

The cellulose materials in this study were commercially available dissolving pulp sheets produced by Domsjö Fabriker (Mw = 570 000 kDa) and Borregaard ChemCell (Mw = 1700 000 kDa). Never-dried, hemi-poor softwood kraft cellulose (Mn = 880 000 kDa) was also used as a starting material. The kraft cellulose was provided by Metsä Group Oy (grade" RMA90", bleached to 90% ISO brightness). Highest grade glycidyl trimethyl ammonium chloride and choline chloride were purchased from Sigma-Aldrich and were dried under vacuum over night at 40 °C and applied immediately after vacuum. Fennopol K3400R and Fennopol K506 are ordinary flocculant grade polyacrylamides, thus their molecular weights are considered to be several million g/mol. Because no accurate methods exist for measuring polyacrylamide molecular weight, their size is commonly characterized by using Standard Viscosity (SV), which is measured from a 0.1% solution prepared with 1 M NaCl with a Brookfield viscometer at 25 °C. Standard viscosity is 3.0 for Fennopol K3400R and 3.8 for Fennopol K506.

2.1. Cationisation of cellulose pulps using conventional methods

Cationisation of cellulose was conducted in heterogeneous form using a similar type of method to that reported by Bendoraitiene et al. [26] for starch by mixing cellulose with catalytic amounts of sodium hydroxide solubilised in water, and glycidyl trimethyl ammonium chloride (GTAC), and stirring the mixture using either a standard mechanical laboratory stirrer or a high viscosity CV Helicone Mix Flow (Design Integrated Technology USA Inc.) high-consistency, high shear mixing reactor, followed by washing and dialysis with water and ethanol. For some samples the cellulose was mercerised similarly to that

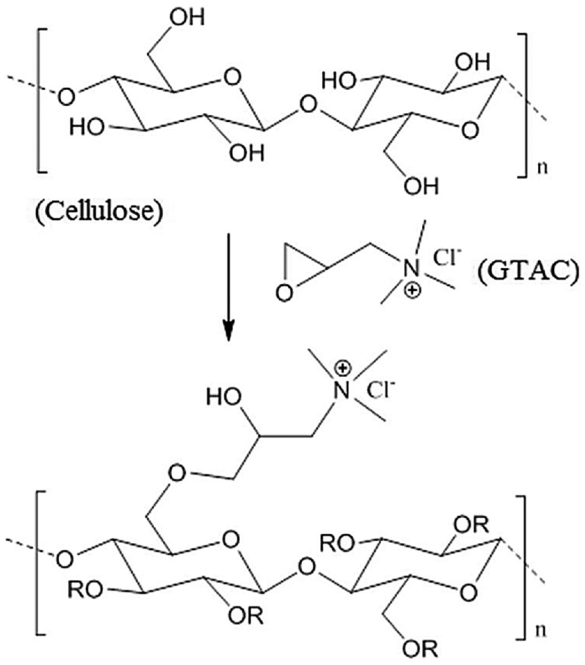

Fig. 1. Cationisation of cellulose using GTAC to produce cationic cellulose, R= H or cationic substituent.

described in the literature [28,29] before the cationisation reaction. Homogeneous cationization reactions of cellulose were conducted using a the method presented by Ott et al. [10], in which cellulose was first solubilised via solvent exchange to dimethylacetamide/5% lithium chloride (DMAc/LiCl) solution and then mixed with GTAC, and NaOH solubilised in water, and the mixture was stirred overnight at the chosen temperature using a standard mechanical laboratory stirrer. The exact parameters for each sample have been presented in detail in the report [9]. The degree of substitution (DS) of the cationic cellulose derivatives was determined based on the nitrogen content of the samples by the Kjehldahl-method [26] and in some cases also additionally using ^{13}C CP/MAS or ^{13}C liquid state spectroscopy. The reaction mechanism for the cationization reactions is shown in Fig. 1.

2.2. Cationisation of cellulose pulps using a deep eutectic solvent (DES) mixture

Cationisation of cellulose was carried out by our previously reported method utilizing a 1:3 mixture of boric acid and glycidyl trimethyl ammonium chloride [18]. In a typical procedure, cellulose (5.0 *g* in dry weight, 70% dry-matter content) was mixed in 100 *g* of the DES solution at 40 °C. After two hours of mixing, 0.16 *g* of sodium hydroxide powder was added to the mixture, and stirring continued for 22 h at a constant temperature under vacuum to remove water. The suspension was washed with water, filtered, and finally dialysed with water and ethanol.

2.3. Application testing of cationic cellulose

Charge density of the samples was measured by titrating the sample at pH 7.5 using a Mütek PCD-03 particle charge detector with 0.001 N sodium polyethylene sulphonate as the titrant. All measurements were repeated five times and reported as the average value of these five measurements. Maximum standard error of the method is 0.01 meq/g. Charge density is considered as the most trustable method to determine cationic charge of cellulose derivatives, because it eliminates the effect of impurities and side reactions, which might influence methods focused in determining the total nitrogen content of the samples. Salt