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The Influence of Modified Starch on the Process Water Quality in Papermaking and the Paper Properties

The influence of modified (cationic) starch on the process water quality in papermaking and paper properties has been investigated. The experiments were conducted on sulfate hardwood pulp by applying both tap and paper mill process water. When process water is used, the retained amount of starch on fibers decreases, which most probably results from a partial neutralization of the cationic charge on modified starch, thereby reducing its attraction to the anionic groups on a fiber. By adding the modified starch, the turbidity of process water is to some extent reduced, indicating that the suspended organic substances are removed from process water. Due to starch accumulation, the load of process water by organic substances (determined via the TOC analysis) is not reduced, but is rather increased when the modified starch is added. In most cases, the addition of modified starch improved the investigated paper properties. However, these properties varied in correlation with the quality of the used water, despite the fact that the dosage of modified starch remained constant. This demonstrates the influence of process water quality, not only on the paper properties, but also on the efficiency of process chemicals, such as the modified starch, in the papermaking process.

Keywords: Retention; Anionic organic detrimental substances; Modified starch; Fibers; Paper properties

1 Introduction

In the paper industry, water is used for the preparation of chemicals, slushing, and diluting of pulp and fillers, their transport to the paper machine, constant application of paper stock onto the paper machine wire, system cleaning, and energy transfer [1]. In addition to fiber particles, fines, and fillers, the process water also contains chemical residues. Due to their undesirable presence in the papermaking process, they are referred to as detrimental substances. Chemically, these substances are inorganic compounds, as well as low-molecular weight and soluble organic substances [2]. With water circuits closing, these detrimental substances begin to accumulate in the process water, which increases the possibility of end product pollution, process equipment corrosion, and slime formation [3, 4]. Their effect on added chemicals is of significant importance as well. Mostly, the detrimental substances of organic origin have a negative surface charge that can influence the consumption of chemicals, since they tend to neutralize their positive charges [5]. The level of detrimental substances can be controlled by fiber washing, which reduces fines, and process water treatment. However, their retention to fibers is also a perfectly acceptable mechanism for removing detrimental substances from the process water [6]. Most of the answers to the questions connected with the accumulation of the above mentioned components in the system should be found in the wet end of the paper machine. Detrimental substances, fillers, and fines are much smaller than fibers, which makes it difficult to retain them in the sheet without adding positively charged cationic polymers [7, 8]. Most frequently in such cases, modified starches are applied [9]. They adsorb onto the surfaces of particles, and thus enable their flocculation into larger clusters that can be retained in a paper sheet.

The properties of paper define its use. Paper properties are mostly determined by the type of fibers and their preparation/treatment. To a certain extent, however, paper properties are also affected by other components of the paper stock mixture, such as fillers and process chemicals. Paper strength is one of the most important properties. It depends on the strength of individual fibers and inter-fiber bonding. Fibers in paper bond with each other via hydrogen bonds between the hydroxyl groups on cellulose and hemicellulose. Although carboxylic groups [10] are the main points for retention of starch to

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fibers, starch can also form hydrogen bonds between fibers and thus strengthen the inter-fiber bonding [11, 12]. Consequently, the mechanical and surface properties of paper are improved as well [13]. Paper properties are also affected by the quality of process water. With water circuit closing, detrimental substances begin to accumulate in the process water and may decrease the quality of the end products [14]. The influence of water circuit closing on paper properties was the subject of numerous studies [9, 14-17]. The published results of studies pertaining to the influence of water circuits closing on the mechanical properties of paper differ quite substantially. Some studies reported negative effects of closing on the mechanical properties, whereas others indicated that these same paper properties are not significantly affected by the circuit closing [15–17, 21–23].

The aim of this study is to determine the influence of modified starch on the quality of process water, both in view of the removal of detrimental substances, as well as the potential accumulation of modified starch in process water. In addition, the effect of the addition of modified starch on the selected paper properties, in both open and closed systems, has been studied.

2 Materials and Methods

2.1 Materials

Cationically modified corn starch with a substitution level between 0.043 and 0.048 (according to the producer Helios d.d., Domžale, Slovenia) was used in this study. In the paper industry, it is used as an additive to the paper stock. Before its application, the solution of modified starch was prepared in accordance with the manufacturer's recommendations. A mixure of water (1 L) and 1 g of modified starch was stirred in a 1-L beaker at 95°C for 30 min. The mixure was cooled to room temperature, and consumed within 6 h.

The experiments were performed with sulfate hardwood pulp (50% birch, 50% poplar) in concentrations of 5 g/L. Before the application, pulp was refined (refiner PFI, refining level 29 SR), and then disintegrated for 15 min at 3000 rpm at a consystency of 5 mg/L.

2.2 Methods

The aim of the experiments was to determine how detrimental substances can affect the retention of modified starch, and what quantity of detrimental substances can be removed from the process water via the modified starch addition. At the same time, the experiments were also conducted in a way that enabled us to monitor the influence of the accumulation of modified starch on the process water quality, as well as the paper properties. The individual experiments were performed in two stages. The tap water was used in the first stage, while the paper mill process water was used in the second. The experiments were performed by means of a laboratory Rapid-Köthlen sheet former machine. The size of a sheet on the former is standardized (a round sheet with a 10 cm radius). The surface of a paper sheet thus amounted to 0.0314 m^2. The basis weight of paper was calculated from the ratio between paper mass and the surface area of the paper sheet. Paper sheets were formed at room temperature and pH 7.5 (Fig. 1).

The amounts of modified starch added were 0, 10, 25, 50 and 75 mg/g of fiber. In the second stage of experiments, process water was used for fiber dilution as well. The modified starch solution applied in the experiments was always prepared with tap water.

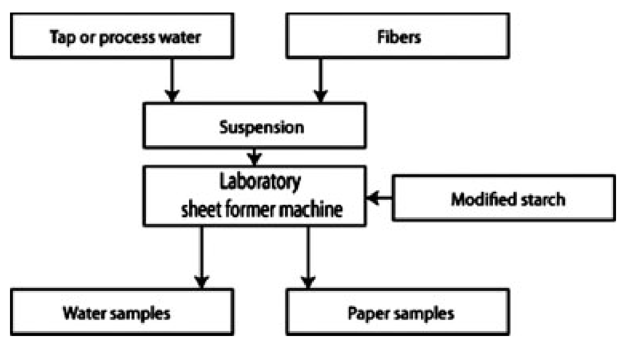

Fig. 1. Schematic of the experimental procedure.

2.3 Analyses

The concentration of modified starch in water was determinated by means of UV/VIS spectrophotometer (Varian Cary, Palo Alto, CA, USA) at 580 nm wavelength, as described by Tappi T419 om-02 method. Turbidity is affected by particles present in the sample. In the papermaking water, these are mostly suspended and colloidal particles. Turbidity measurements were conducted by means of the HACH DR/2000 spectrophotometer (Hach, Loveland, CO, USA) at 450 nm wavelength (ISO 7027).

TOC was used for determination of carbon content in the soluble and colloidal organic substances within the sample. TOC measurements were conducted on a Shimadzu TOC-V analyzer. Before the analysis, the suspended substances were removed from samples by means of filtration through a glass filter (SIST ISO 8245).

The surface charge (SCD) was determined by titration on a Kolb-SSD-1000 detector. This method is based on the neutralization of polyions with an oppositely charged polyelectrolyte. The surface charge of a sample is calculated (in eq/L) from the volume consumption of a polyelectrolyte with known mass concentration and surface charge. The anionic polyelectrolyte applied was potassium polyvinylsulfate (Merck, Darmstadt, Germany), with molar mass 162 g/mol, at a concentration of 0.162 g/L, which corresponds to a 10^{-3} M solution. Polydiallyl dimethyl ammonium chloride (PDADMAC) calibrated with polyvinylsulfate was used as the cationic polyelectrolyte in SCD titration.

Before the analyses, sample paper sheets were conditioned at 23°C and 50% relative humidity for 24 h (SIST ISO 187 standard).

The basis weight of samples was measured according to the SIST ISO 536 standard, and has varied (up to 5%) within an individual experiment. Therefore, the values of mechanical properties are presented in the form of indexes, defined as the value measured divided by the basis weight of a sample.

Tensile strength was tested by the Alwetron TH1 tensile tester (Lorentzen & Wettre, Kista, Sweden) in accordance with ISO 1294-2. The tear resistance measurements were conducted on a Lorentzen & Wettre tear resistance tester in compliance with ISO 1794.

Delamination gives a measure of the inner strength of a paper sheet. The measurements were conducted on a Scott internal bond tester (IBT) (analitest, Ft. Lauderdale, FL, USA) according to Tappi 569 method.

$Cobb_{60}$ is a method for determining the amount of water absorbed by 1 m^2 of paper surface in 60 s. The smaller the $Cobb_{60}$ values, the lower the amount of water that penetrates into the fiber network, which indicates a higher hydrophobicity of paper. Paper sizing was studied with the $Cobb_{60}$ method (ISO 535).

3 Results and Discussion

Analyses of the process water (from the production of graphic paper), presented in Tab. 1, show the characteristics of both waters used in this study. As expected, the tap water turbidity is 0 FTU. The process water turbidity, however, results from the accumulation of organic and inorganic colloidal substances. The SCD values show that these substances are negatively charged, which causes the electrostatic attraction between them and the cationic polyelectrolyte (modified starch). The tap water also carries a certain, though very small, negative charge. This can be explained by the TOC analyses, which show that a certain amount of organic and inorganic soluble substances is present in the tap water as well. The quantity of organic substances is understandably much higher in the process water, due to the presence of fiber particles, fines, and residues of organic chemicals. All of them tend to increase the TOC values, including the starch, which remains in water partly as a chemical residue (modified starch), and partly as a component of the coating mixture entering process water with broke. With regards to its SCD values, the modified starch in water carries a cationic charge that is partly or completely neutralized with the suspended substances in the process water.

Tab. 1. The characteristics of water used in the experimental work.

	TOC (mg/L)	Turbidity (FTU)	SCD (μeq/L)	starch (mg/L)
Tap water	60	0	(−)0.1	0
Process water	340	262	(−)0.815	50

Fig. 2 shows the dependence of the retention of modified starch on the initial starch concentration in the solution. The difference in the binding is evident in the case of applying the tap water. If starch already present in the process water is included in the initial concentration of starch in water, we obtain the dependence of the retained amount with regards to the total concentration of starch in water. Thus, the retention of total starch on fibers is understandably lower in the case of process water. The surface-neutralized starch that is present in process water can be bound to the fiber surface either by means of an anionic detrimental substance with which it forms a complex, or via dispersive (hydrophobic) interactions between its own alkyl chains and those of the cellulose, but not via electrostatic interactions. The binding of the complex, however, depends on the surface charge and the frequency and efficiency of collisions between the complex and modified starch and the fiber. At the same time, the charge of added modified starch is partly neutralized by anionic detrimental substances in process water, consequently decreasing its affinity for fibers.

3.1 Influence on the process water properties

The slight increase of the SCD value in the process water, which is shown in Fig. 3, results from a partial charge neutralization of modified starch, as well as from the retention of detrimental substances to fibers. When tap water is used instead, the negative surface charge of colloids is quickly neutralized, and the positive charge

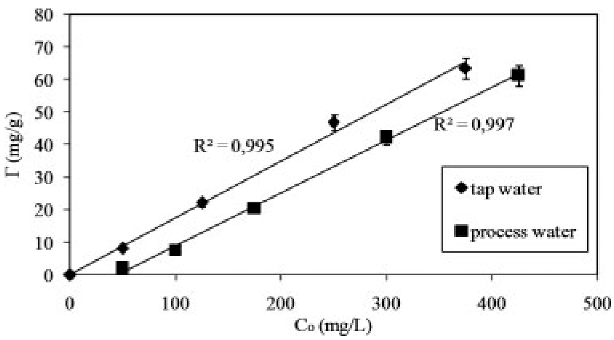

Fig. 2. Dependence of the mass of modified starch retained per unit of fiber mass on the concentration of starch in water.

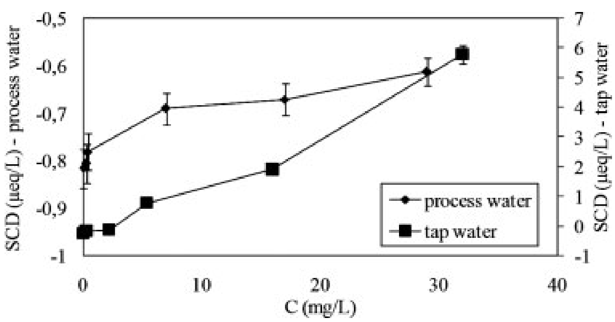

Fig. 3. Dependence of SCD values on the modified starch concentration in water.

becomes prevalent, thus causing the repulsive forces among the individual segments on modified starch to increase. The growth of SCD values tends to change from negative to positive values already at 5 mg/L concentration of modified starch in the tap water. When process water is used, on the other hand, SCD values remain negative even at higher concentrations of modified starch (up to 30 mg/L). Both the retained amount (Fig. 2) and the SCD analyses (Fig. 3) indicate that the modified starch has a higher affinity for retention to fibers and fines than for charge neutralization with the detrimental substances. This is most probably caused by a higher surface charge on the fibers, and the size of the fiber itself, since it is much more likely that a collision will occur between a polymer chain of the modified starch and a relatively large fiber molecule, than a comparatively very small suspended anionic detrimental substance.

Starch, even in its unmodified, and hence uncharged, "native" form, can also retain onto the cellulose fiber surface via the dispersive interactions between the non-polar segments of its own polymer chain and those of the cellulose. This effect, however, can only become appreciable when the lateral repulsion between the charged segments becomes low enough to accommodate such hydrophobic association: in high ionic strength solutions (high electrostatic screening), and/or when the excess surface charge on the chains is at least partly neutralized by the retention of oppositely charged components. Consequently, some retention of starch on the cellulose fibers is observed even with completely uncharged starches. This effect can be deduced by comparing Figs. 2 and 3. While the SCD value of the process water remains fairly constant, at least when compared to the SCD of tap water, throughout the whole range of initial starch concentrations, due to the surface charge neutralization with the detrimental anionic components present in considerable amounts in the process water, the retained amounts of starch in both waters do not differ so much. This indicates that the adverse effect of partial surface charge neutralization of starch in the process water is partly offset by the both alternative mechanisms of starch retention.

Modified starch reduces the process water turbidity. The decrease in turbidity indicates the destabilization of suspension, i.e. particles in the process water are being integrated into larger structures. Fig. 4 shows that very small amounts of modified starch drastically reduce the turbidity of process water. With higher additions, the turbidity ceases to decrease, which is most probably due to the fact that the complexes formed are no longer bound to fibers, but rather remain in the process water. In the case of tap water application, the turbidity has increased only slightly with the addition of starch: from 0 to 10 FTU. This slight—and from the minimum point on the tap water turbidity curve also completely comparable in magnitude— rise of the turbidity in both waters used in the study shows that the starch macromolecules themselves are still too small to significantly affect the solution turbidity. The signicantly higher turbidity of the process water at high starch dosages, on the other hand, demonstrates the continuing presence of dispersed colloid associated complexes in the solution.

The retention efficiency of modified starch on fibers is reduced in concert with the increase of its concentration in solution. As a consequence, the modified starch starts to accumulate in the process water, thereby enhancing the load of process water with organic substances, and, consequently, also causing higher TOC values. This is especially evident (see Fig. 5) in the case of tap water application, where the TOC values with starch present in water increase from 50 to 150 mg/L. If process water is used, the TOC values also reflect the presence of organic detrimental substances in water. The initial additions of modified starch cause the organic detrimental substances to be partly retained on starch and consequently to fibers, which reduces the TOC values as well. With higher amounts of added starch, the organic detrimental

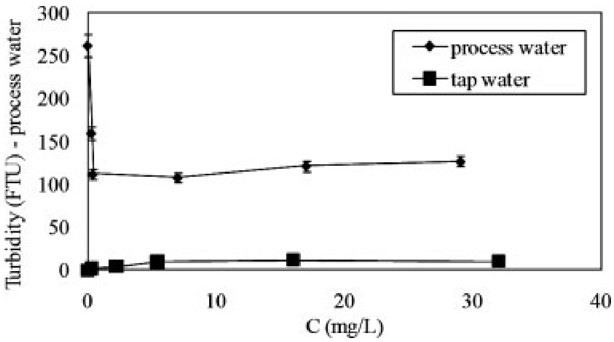

Fig. 4. Dependence of turbidity on the modified starch concentration in water.

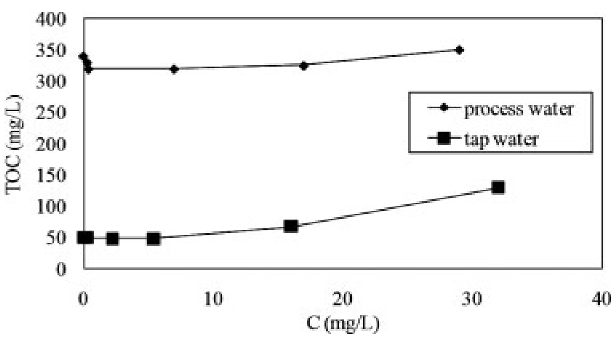

Fig. 5. Dependence of TOC on the modified starch concentration in water.

substances are also removed from the system. However, since the concentration of modified starch in process water increases, the TOC values also grow. This hypothesis has been confirmed with an experiment, whereby tap water was used, and the TOC values increased in conjunction with the concentration of modified starch present in water. When process water is used, the higher TOC results from the presence of organic substances. It can thus be concluded that only a relatively small amount of organic detrimental substances is removed from the process water by the addition of modified starch.

3.2 Influence on the paper properties

The tear is a paper property that depends mostly on the fiber characteristics, such as the number of fibers in a structure, fiber length, and coarseness. Previous research indicated that the tear remains constant with water circuit closing [15]. Fig. 6 shows that the tear index of a paper sheet, formed in the tap water without additions, amounts to approx. 9.7 mNm^2/g, and decreases to 8.5 mNm^2/g, when the process water is used. Both in the first and second series of experiments the tear index decreased with increasing amounts of retained modified starch. This

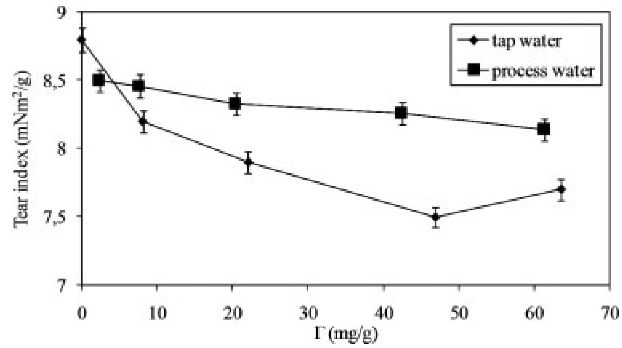

Fig. 6. Dependence of the tear index on the relative concentration of starch retained on fibers.

could be due to higher retention of fines in paper, which lowers the coarseness and decreases the tear. When process water is used, a smaller amount of starch is retained on the fibers or is bound to fibers in the form of complexes, which increases the rigidity of fibers and reduces their tear resistance [18]. The initial value is higher when the tap water is used. However, the tear index values remain constantly lower in the tap than in the process water, which demonstrates the importance of process water quality for the fiber rigidity.

Tensile strength is one of the properties that are frequently used for studying the influence of additives on paper strength [12]. Tensile strength depends on the strength of fibers themselves, as well as on the quantity and quality of inter-fiber bonds [18, 19]. In both series of experiments, the tensile index increased (Fig. 7) with increasing additions of modified starch, which indicates the importance of starch contribution to inter-fiber bonding and, consequently, also to paper strength [15, 20]. When process water is used, values for the tensile index are slightly lower, which may be caused by a somewhat lower retention of modified starch, and by the presence of other substances in the process water that can affect the inter-fiber bonding. The tensile index increases in a "closed" water circuit as well, in agreement with previously published research [9].

Similar results were obtained for delamination (i.e., the IBT values), which is the criterion for the inner strength of a paper sheet. Like the tensile strength, the inner strength depends on the quality of inter-fiber bonding. As can be seen from Fig. 8, increase in the retained amount of modified starch results in strengthening of the inter-fiber bonding. When process water is used, IBT values are significantly higher than with the use of tap water. In both cases, however, IBT values increase very similarly in concert with the increasing amounts of starch retained. The slight difference can be attributed to the detrimental substances in the process water that additionally con-

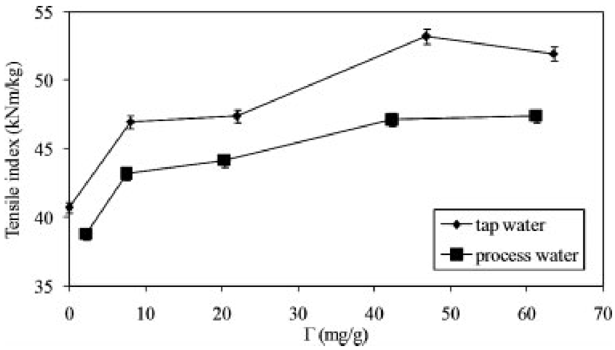

Fig. 7. Dependence of the tensile index on the relative concentration of starch retained on fibers.

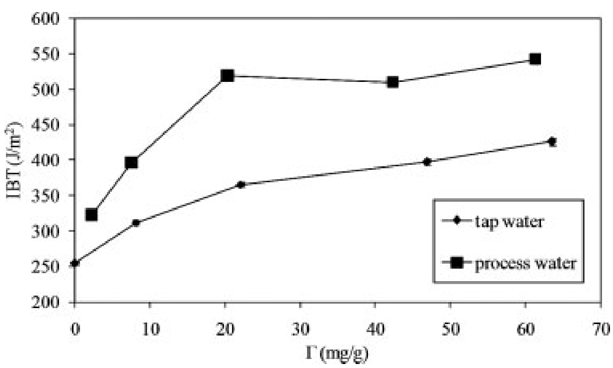

Fig. 8. Dependence of delimination (IBT values) on the relative concentration of starch retained on fibers.

tribute to inter-fiber bonding in the paper sheet structure (process chemicals residues).

The surface properties of paper are especially important for printing papers, because they determine the penetration of water and ink into the fiber network. In order to avoid such an effect, the fiber surface, which is naturally hydrophilic in nature due to the presence of polar groups on fibers, has to be properly treated. The surface sizing effect, i.e. the imparting of the desired hydrophobic character to the cellulose fiber surface, is generally achieved via the retention of various amphiphilic polymers. For this purpose, the process chemicals known as sizes are used. Their task is to prevent the penetration of water into the fiber pores, meaning that the surface is coated with a layer of size [24]. To a certain extent, such effect can also be achieved with other process chemicals (polymers) being retained on the fiber surface. Commonly encountered $Cobb_{60}$ values for the printing paper range between 20 and 25. Fig. 9 shows a $Cobb_{60}$ value of 120 for paper made with the tap water and without additives. A small addition of modified starch already increases the paper hydrophobicity, and the $Cobb_{60}$ values fall below 100. However, the $Cobb_{60}$ values do not fall below 80 even at high additions. A similar effect can be observed in the process water: the $Cobb_{60}$ values decrease with increasing additions of modified starch in approximately the same ratio as in the tap water. Lower values compared with the tap water are understandable, because the residues of size in the process water also retain on the fiber surface. The results demonstrate that modified starch also contributes to the "closing" of fiber surface. However, as can be seen from the $Cobb_{60}$ values obtained at high starch dosages, it can merely represent an addition to the sizes, not their substitute.

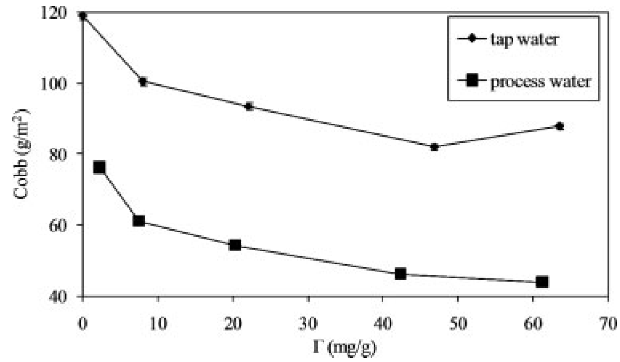

Fig. 9. Dependence of paper sizing ($Cobb_{60}$ values) on relative concentration of starch.

4 Conclusions

The results of this study demonstrate how the detrimental substances present in the process water influence the binding of modified starch on the cellulose fibers. They partially neutralize the charge of the modified starch, thus reducing the attraction between the anionic head-groups on the fiber surface and the cationic groups on starch. The partial neutralization is indicated by the increase in SCD values in the process water, which, however, is also a consequence of the retention of anionic detrimental substances on the fibers. The positive effect of adding the modified starch is evident in the case of process water turbidity. TOC values tend to decrease slightly after the first small additions, but quickly return to their initial state or even increase with increasing starch concentration in the process water. It can therefore be concluded that in the experiments conducted on a laboratory sheet former machine, only the suspended substances are removed from the process water, but not the soluble and colloidal substances, which not only prevents any significant decrease of the process water load with organic substances, but even causes this load to increase due to the accumulation of starch.

Paper properties are affected by both the addition of modified starch, and the quality of water used. Only the tensile index is adversely influenced by the addition of starch. Other mechanical properties of paper improved when the modified starch was added, which demonstrates its contribution to the inter-fiber bonding. The retention of starch on the fibers contributes to the closing of fiber surface as well, hindering the penetration of liquid into the fiber pores, and increasing the hydrophobicity of the paper surface. The differences between the results obtained with the tap and the process water are related to the quality of process water, defined by the type and method of paper production.

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