

REMOVAL OF DETRIMENTAL SUBSTANCES FROM PAPERMAKING PROCESS WATER BY THE USE OF FIXING AGENTS

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Abstract

Detrimental substances are a group of various dissolved and colloidal anionic oligomers or polymers and non-ionic hydrocolloids in papermaking waters, which negatively affect the papermaking process during the reusal of process water. They can be removed from the process water by the use of fixing agents (chemicals with high surface charge density). In our work we investigated the efficiency of detrimental substances removal by the use of Al-salt, combined with a polyelectrolyte. The results showed that in this way the detrimental substances could be removed quite well. Also it was found, that the removal efficiency is not dependent only on fixing agent concentration, but also on other factors.

Introduction

Beside the positive effect of reducing the fresh water consumption, the water loop closure in the papermaking process also has some negative effects. One of them is the accumulation of the so-called detrimental substances (“anionic trash”) in process water.

The term detrimental substances is a common name for various dissolved and colloidal anionic oligomers or polymers and non-ionic hydrocolloids from various sources: ^{1,2}

- raw materials (pulp) are the source of lignin and lignin-like compounds, hemicelluloses, as well as “wood extractives”,
- recycled paper is the source of synthetic sticky components (“stickies”),
- additives are the source of polyphosphates and polyacrylates,
- process chemicals residues are the source of starch, sizing agents, retention aids, biocides and dispersants,
- fresh water is the source of humic acids.

Although some of the above-mentioned substances (additives and process chemicals) are necessary in the papermaking process, all of them negatively influence the same process if they are present in concentrations that are too high. Most frequent problems caused by detrimental substances are:

- formation of deposits on process equipment and appearance of spots on paper sheet,
- reduction of process chemicals efficiency and consequential decrease of retention,
- reduction of paper quality (whiteness, strength, opacity, spots and holes in paper sheet...),
- negative effects in final stage of process water treatment.

In general, there are two possibilities for removing detrimental substances from the process water. The first possibility is their precipitation combined with flocculation. Flocks formed during this process are then separated by microflotation or filtration. Detrimental substances removed in this manner can no longer interfere with the papermaking process. At this point, two conditions should be taken into account. Firstly, the concentration of detrimental substances must be sufficiently high to ensure economical efficiency of precipitation. Secondly, the “mixture” should be appropriate for removal by precipitation.³

The second possibility is fixation of detrimental material (by the help of proper chemicals) and their removal with the paper sheet. The mechanism of fixation is rather complicated, but there are some general ideas of how the fixation process takes place. Characterisation of detrimental substances shows that they consist of dissolved substances (about 10%), and of particles sized between 1 μm and 50 μm (about 90%), in most cases with strong anionic charge on the surface.^{4,5} Because fibre surface is also negatively charged, fixing agents (in most cases organic polymers) must have a highly positive surface charge to achieve fixation. The first stage of fixation mechanism is probably the precipitation of dissolved detrimental substances, combined with flocculation of colloidal particles to form polyelectrolyte complexes with the fixing agent.⁴ In the second stage, these complexes can either be removed by filtration effect in the fibre mat (paper sheet), or they can be adsorbed on fibre surface and then removed along with fibres. Which of the above-mentioned mechanisms will occur depends on the overall surface charge balance in the system. If the overall surface charge on the formed complex is neutral, the removal will occur only by filtration, but if the overall surface charge is positive,

adsorption on fibres (with negative surface charge) can also occur.⁵ Beside the surface charge density, and the type and molecular structure of the fixing agent, surface properties of fibres influence the efficiency of fixing process as well.⁶

Experimental

SAMPLE PREPARATION

The basic sample for our experiments was a suspension of unbleached stone groundwood (SGW) pulp, obtained directly from an industrial size grinder. The pulp concentration in suspension was about 4%. This type of pulp was chosen because of its high content of wood extractives which represent one of the main groups of detrimental material.^{7, 8, 9} The sample was diluted with fresh water to 1% concentration and stirred for 10 minutes. Then, the fixing agent was added (in desired concentration) during continuous stirring. Afterwards the suspension was stirred for another 10 minutes. Then, it was filtered through 100 µm screen, and one part of the filtrate was analyzed. The rest of the filtrate was centrifuged at 3000 rpm for 20 minutes, and the obtained centrifugate was subsequently analyzed in the same way as the filtrate.

FIXING AGENTS

The applied fixing agents were made as combinations of poly-aluminum chloride (PAC) solution with polyelectrolytes. Two different polyelectrolytes have been used. One was a polyamine (PAM) type polyelectrolyte and the other was a poly-diallyldimethylammonium chloride (poly-DADMAC) type polyelectrolyte. Each of them has been mixed with the poly-aluminum chloride solution in several different proportions (all mixtures were supplied by Belinka, Kemična tovarna Moste). The fixing agent manufacturer did not approve publishing of more detailed information about the polyelectrolytes. After the most efficient fixing agent was determined (which will be described later), it has been added to the pulp suspension in various quantities (from 50 ppm to 800 ppm) to determine the dependence of its effects from its concentration.

ANALYTICAL METHODS

The presence of detrimental compounds was determined by measuring the following parameters:

- pH value,
- conductivity,
- turbidity,
- charge demand,
- COD value,
- dissolved matter,
- solid matter,
- resin acids concentration,
- lignin concentration,
- total carbohydrates concentration.

Turbidity was measured in Formazin Turbidity Units (FTU) on the HACH DR/2000 spectrophotometer.

Charge demand (surface charge density) was determined by polyelectrolyte (neutralization) titration, performed with the streaming current detector (Kolb-SSD-1000) combined with automatic titrator (Mettler DL21). The results are presented in microequivalents of charge per litre of sample.

COD value was determined according to ISO 6060 (1989) standardized method.

Dissolved solids and total suspended solids were determined gravimetrically.

After the extraction with methyl-t-butyl ether, the concentration of resin acids in organic phase was determined chromatographically (on Hewlett Packard HP 5890 gas chromatograph), and the concentration of lignin in water phase was measured spectrophotometrically (on Varian CARY 50 UV/VIS spectrophotometer).⁹

Total concentration of carbohydrates was also determined spectrophotometrically after the reaction with orcinol (colour reagent) on Varian CARY 50 UV/VIS spectrophotometer.

Results and discussion

Because the main reason for using fixing agents is to remove the detrimental substances from process waters, some of the obtained research results are presented as removal efficiency, simply defined in the following formula:

$$\text{efficiency [\%]} = \left(1 - \frac{\text{value of the chosen parameter after fixing agent was added}}{\text{value of the chosen parameter without fixing agent addition}} \right) \cdot 100$$

The experiments were performed in two parts. In the first part, different fixing agents were tested in order to choose the most efficient one. In the second part, the most efficient fixing agent was taken to determine the concentration dependence of the efficiency and the optimal fixing agent addition (a similar experiment was performed by some researchers with another fixing agent in a suspension of thermomechanical pulp).¹⁰

DETERMINATION OF THE MOST EFFICIENT FIXING AGENT

In a series of fixing agents which differed according to the concentrations of the polyelectrolyte added to Al-salt solution, we tried to determine the most efficient one. For this purpose, the results (tables 1 and 2) obtained in an experiment of adding 200 ppm of fixing agent (calculated relative to the total mass of suspension) to the pulp suspension were used.

There was no significant change of pH value and conductivity after the addition after the addition of 200 ppm of fixing agent. pH value obtained approximately 7.8 (± 0.1), and the conductivity level was around 440 (± 10) $\mu\text{S/cm}$.

The most effective is fixing agent no. 2. It shows fairly good removal efficiencies for the majority of selected parameters. Because the results in tables 1 and 2 refer to the centrifugate, it can be established that only dissolved and colloidal matter is present. Therefore, a conclusion can be drawn that a remarkable amount of detrimental substances has been removed. The reduction of turbidity indicates a removal of colloid particles. The reduction of charge demand in combination with COD reduction indicates the removal of negatively charged organic particles, which meet the definition of detrimental substances. At this point it should be noted, that the removal of wood extractives (although they are present in low concentrations) significantly contributes to COD

reduction.^{7,8} Low removal efficiency of dissolved and non-dissolved substances can be explained by the fact, that these two parameters include both organic and inorganic substances, but fixing agents remove mostly organic detrimental substances.

Table 1. Measured values of various parameters with and without fixing agent added.

<i>Fixing agent sample no.</i>	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>6</i>	<i>original sample*</i>
<i>Amount of polyelectrolyte in the fixing agent [%]</i>	0	1.0 [†]	0.8 ^{††}	0.5 [†]	0.5 [†]	0.8 ^{††}	/
<i>Cationic charge [meq/g]</i>	0.203	0.223	0.232	0.161	0.193	0.348	/
<i>Turbidity [FTU]</i>	49	35	32	44	70	47	98
<i>Charge demand [μeq/L]</i>	145	129	125	160	172	175	251
<i>COD [mg/L]</i>	315	308	304	315	331	307	385
<i>Dissolved solids [mg/L]</i>	412	416	436	457	434	464	514
<i>Total suspended solids [mg/L]</i>	39	34	47	39	35	32	44
<i>Resin acids [mg/L]</i>	2.2	3.1	2.4	5.4	2.8	4.2	8.5
<i>Lignin [mg/L]</i>	56	60	58	56	52	52	80
<i>Total carbohydrates [mg/L]</i>	78	79	80	58	55	52	87

[†]PAM; ^{††}p-DADMAC; * pulp suspension, 1% concentration

Table 2. Removal efficiencies of different fixing agents.

<i>Fixing agent sample no.</i>	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>6</i>
<i>Amount of polyelectrolyte in the fixing agent [%]</i>	0	1.0 [†]	0.8 ^{††}	0.5 [†]	0.5 [†]	0.8 ^{††}
<i>Cationic charge [meq/g]</i>	0.203	0.223	0.232	0.161	0.193	0.348
Parameter	Efficiency (%)					
<i>Turbidity</i>	50	64	67	55	29	52
<i>Charge demand</i>	42	49	50	36	31	30
<i>COD</i>	18	20	21	18	14	20
<i>Dissolved solids</i>	20	19	15	11	16	10
<i>Total suspended solids</i>	11	23	0	12	20	27
<i>Resin acids</i>	74	64	72	36	67	51
<i>Lignin</i>	30	25	28	30	35	35
<i>Total carbohydrates</i>	10	9	8	33	37	40

[†]PAM; ^{††}p-DADMAC

Similar results were obtained by samples that were only filtered through a 100 μm screen, although these samples contained some fibre residuals and fines.

The results presented by table 2 also indicate that the efficiency of a fixing agent is not necessarily dependent on its cationic demand. This phenomenon is probably due to the molecular structure of the polymer used.⁵

INFLUENCE OF THE FIXING AGENT CONCENTRATION

The fixing agent no. 2, which proved to be most efficient, was used to determine the influence of its concentration on the removal efficiency. For this purpose, various amounts of the fixing agent (from 50 to 800 ppm) were added to the fibre suspension. Again, all the above-mentioned parameters were measured, and the results are shown in Fig. 1 – 6.

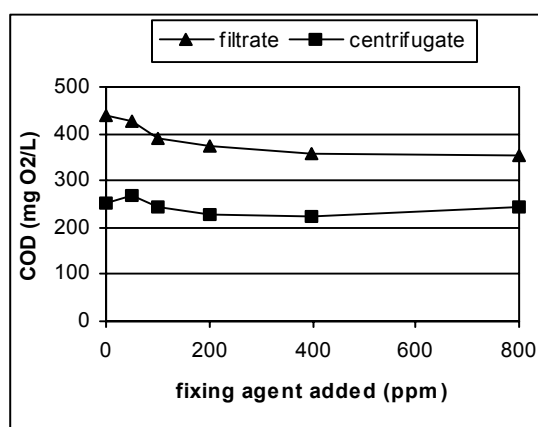


Fig 1. Dependence of COD on the amount of fixing agent no. 2 added

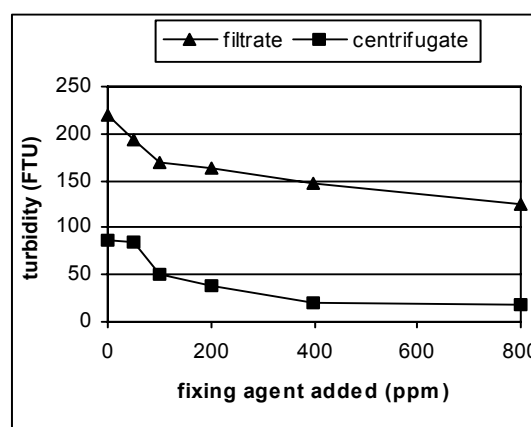


Fig 2. Dependence of turbidity on the amount of fixing agent no. 2 added

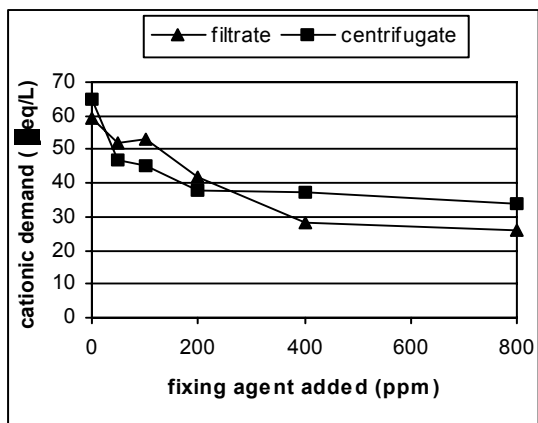


Fig 3. Dependence of cationic demand on the amount of fixing agent no. 2 added

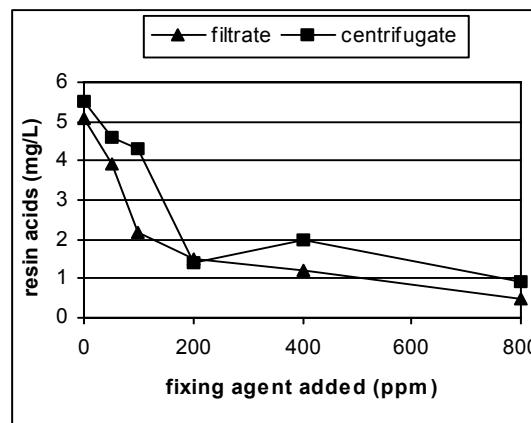


Fig 4. Dependence of resin acids concentration on the amount of fixing agent no. 2 added

Although the values of all parameters for the original sample (0 ppm in Fig. 1 – 6) are somewhat lower compared to the first experiment, the removal efficiency (if calculated) at 200 ppm is almost the same.

With increasing amount of fixing agent, pH value decreased from 7.5 (at 50 ppm) to 6.7 (at 800 ppm). Similarly, conductivity increased by almost 20% (from 415 to 495 $\mu\text{S}/\text{cm}$), especially between 400 to 800 ppm of fixing agent added. The reason for this

change is probably due to the fact that one of the constituents of the fixing agent is aluminium salt which causes higher conductivity in excess.

A decrease of COD value, turbidity and cationic demand (fig. 1, 2 and 3) indicates a removal of colloidal organic matter. These results, combined with the results of resin acids (fig. 4), lignin and total carbohydrates (fig. 5) concentration measurements, are in accordance with suggestions of some authors¹¹ claiming that wood components are adsorbed on the surface of colloidal particles. Therefore, if colloidal particles are

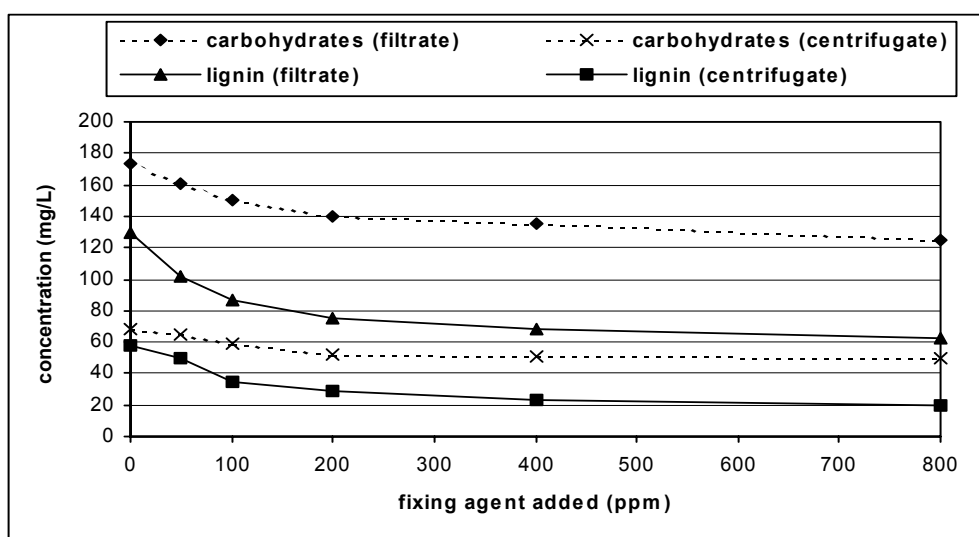


Fig 5. Dependence of carbohydrates and lignin concentration on the amount of fixing agent no. 2 added.

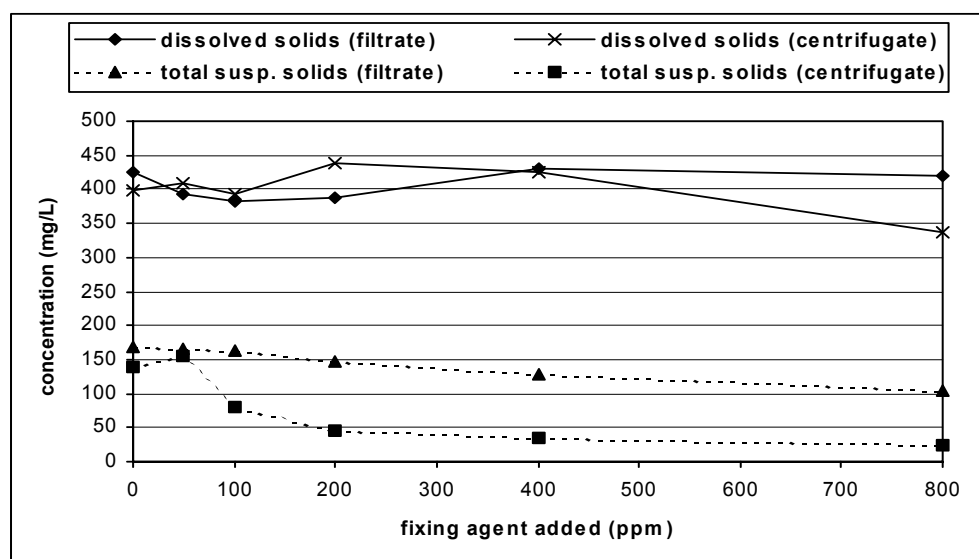


Fig 6. Dependence of dissolved solids and total suspended solids concentration on the amount of fixing agent no. 2 added.

removed by fixation, this should also result in reduction of lignin, total carbohydrates and resin acids concentration, which proved to be the case in this particular research.

It can be seen that all but one of the measured parameters decrease in proportion with an increasing amount of fixing agent added. The exception is the concentration of dissolved solids (fig. 6) which decreases at lower fixing agent additions, but when a fixing agent of over 200 ppm is added, it starts to increase slightly, which is possibly caused by the overdosage of fixing agent. However, this should be confirmed by further research.

It is evident from Fig. 1 – 6 that the decrease in measured parameters is not linearly dependent on the amount of fixing agent added. The minimum value is reached rather soon, between 200 and 400 ppm, which is probably due to the stabilization of colloidal particles at higher fixing agent additions. According to the mechanism proposed by some authors,^{4,5} high concentrations of fixing agent primarily cause precipitation, flocculation, and probably also adsorption on fibres with a predominantly negative surface. However the shearing forces (due to mixing) can cause desorption from fibres, and the excessive fixing agent stabilizes the desorbed particles. Despite the excess of negative charge in the system, an increase in amount of fixing agent added only lowers the charge demand of the suspension, but does not increase the removal efficiency. It can be concluded that the major part of fixing agents efficiency is expressed already at lower concentrations of fixing agent, and that additions which exceed 200 ppm are not quite justified. Although it should be noted that, for different fixing agents, this optimum dose could vary depending on the type and composition of the agent.

Conclusions

Fixation is an efficient method of removing detrimental substances from papermaking process waters. It shows fairly good results due to removing colloidal material and soluble wood components. The removal of colloidal material can be assumed because of a significant decrease in turbidity. Wood components (lignin, resin acids) are also removed quite well by fixation (which is evident from the results of our analyses). Due to their significant contribution to COD value, COD value is also reduced by

approximately 20%. If the results are shown in terms of efficiency, it can also be seen that the removal efficiency does not depend on cationic demand of the fixing agent only, but also on the type (and structure) of the polymer in the agent. Therefore it can be concluded that the surface charge density of the fixing agent cannot be used as a simple criterion for its efficiency. With increasing concentration of the fixing agent, its efficiency does not increase constantly (in a linear way), but reaches a certain maximum. The majority of the fixation effect is expressed already under 200 ppm of fixing agent added. Apparently, with over 200 ppm of fixing agent added, stabilization of colloidal particles occurs and there is no significant increase in efficiency. For this reason, the use of fixing agents in higher concentrations is not quite justified (especially because of their price). The optimum addition of fixing agent varies with its type. As proved by our research, it was somewhere around 200 ppm for the selected fixing agent.

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Povzetek

Moteče snovi je skupno ime za različne raztopljene in koloidne anionske oligomere ali polimere ter neionske hidrokoloide v papirniških vodah, ki pri ponovni uporabi procesne vode negativno vplivajo na proces proizvodnje papirja. Iz procesne vode jih je možno odstraniti z uporabo fiksirnih sredstev (kemikalij z visoko gostoto naboja na površini molekul). Naše delo je obsegalo ugotovitev učinkovitosti odstranjevanja motečih snovi z uporabo Al-soli v kombinaciji s polielektrolitom. Rezultati so pokazali, da je na ta način možno odstraniti moteče snovi v zadovoljivem obsegu. Ugotovili pa smo, da učinkovitost odstranjevanja ni odvisna samo od koncentracije fiksirnega sredstva ampak tudi od drugih dejavnikov.