Application of ultrafiltration in the pulp and paper industry: metals removal and whitewater reuse

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Abstract

In the pulp and paper industry, the water use minimization is a constant target. One way to reduce water use is to recycle the effluent in a closed-cycle concept. In paper mills, the main source of liquid effluent is the so-called whitewater, which is the excess water, originated from pulp stock dewatering and other fiber contaminated water. This research studied the reuse of paper mill whitewater after membrane ultrafiltration (UF) in the paper machine and in the pulp bleach plant of an integrated mill. Contaminant removal and flux behavior of the UF system were evaluated. The treatment by ultrafiltration was technically feasible and the treated whitewater had good potential to be reused in some processes in the paper machine. The reuse of ultrafiltered whitewater in the bleaching plant was not recommended because of the high level of soluble calcium present in this stream. Therefore, a combined treatment of the whitewater using the principle of precipitation and ultrafiltration was proposed showing good results and enabling the use of the treated whitewater in the bleach plant.

Keywords: Ultrafiltration; water reclamation; whitewater reuse; kraft pulp and paper mills; hardness removal

1. Introduction

In the pulp and paper industry, minimization of water consumption can be achieved by recycling effluent in a closed-cycle concept (Silva, 1997, 2001; Wörster and Costa, 1997). However, the reuse of raw effluent in some processes is not always feasible due to its poor quality and, therefore, a prior treatment to remove specific contaminants for reuse is required. In the pulp and paper production, some problems can occur if the effluent is not previously treated. These problems are related to the degradation...
of pulp and paper quality, the formation of deposits and scales, the severe corrosion of equipments and pipes, and the increase on chemicals consumption.

Currently, water consumption in paper mills ranges from 10 to 30 m$^3$/t (Wörster and Costa, 1997), depending on the type of paper produced and on the water circuit of the paper machine. Often, the reclamation of water is only possible if prior treatment to remove contaminants is applied.

Some researchers have been working on membrane separation processes for paper machine whitewater reclamation (Silva et al., 1999; Jokinen et al., 1995; Jokinen et al. 1993) with promising results. Benefits such as fresh water consumption minimization, chemicals use reduction, fiber loss and pollutant generation decrease can be achieved by whitewater reuse (Silva, 2000).

In the production of bleached kraft pulp, an important water consumer and effluent producer is the bleach plant. The water quality to wash the pulp after each bleaching stage is crucial to prevent problems related to the pulp quality and equipment deposits, scaling and corrosion. The use of paper mill whitewater on the bleaching washers is limited by the high concentration of calcium, which can cause deposits and scales of calcium oxalate and calcium carbonate. Therefore, the use of whitewater in the bleach plant would be facilitated if calcium ions are previously removed.

The objectives of this research were:

i) Study the technical viability of whitewater reclamation in the paper mill after membrane ultrafiltration in a pilot plant.

ii) Propose a new method for removing calcium and magnesium from the effluent in order to enable whitewater reclamation in the pulp bleaching plant.

iii) Investigate the effect of the reuse of whitewater in the bleach plant on paper quality and on the filtrate quality.

2. Whitewater reclamation in the paper mill after membrane ultrafiltration

2.1. Material and Methods

2.1.1. Whitewater

The whitewater samples used in this study came from an integrated kraft bleached pulp and paper mill. The samples were collected from the whitewater tank that is used for dilution of the bleached pulp entering the paper machines. Figure 1 shows a schematic of the integrated mill and the sampling point.
2.1.2 Experimental

Whitewater treatment was carried out in a ultrafiltration (UF) pilot plant as showed in Figure 2. Whitewater treatment was carried out in a ultrafiltration (UF) module system as showed in Figure 2. A submerged ultrafiltration hollow-fiber module was used for the filtration experiments. This system consists of a bundle of hollow-fiber ultrafiltration membranes submerged in a tank, into which the effluent is introduced. Each hollow fiber was approximately 2 mm outside diameter and 1.0 m long. The total membrane area was 1 m\(^2\). Membrane fibers were assembled in such a way that they were free to move. Transmembrane pressure was provided by an external pump, which created a vacuum inside the fiber lumen, generating a flux from the outside to the inside of the hollow fiber. A transmembrane pressure of -33.8 kPa (-10 in Hg) was used. Aeration was used to promote turbulence to minimize concentration polarization and fouling. Air was injected using an air blower. The air flow was kept at 0.48 L.s\(^{-1}\). The tank had a diameter of 0.4 m and a volume of 120 L. Polymeric hydrophilic membranes with a nominal pore size of approximately 0.02 µm were used.

The experimental apparatus design allows changes in transmembrane pressure and air flow. Backflushing was carried out by reversing the flux of permeate. This was accomplished by changing the flux automatically using solenoid valves and a timer. The operation was automatically made in cycles of filtration (15 minutes) and reverse filtration (30 seconds).
Whitewater ultrafiltration was carried out batchwise in three cycles. In each cycle, the system operated continuously during 8 hours, where 100 L of whitewater were treated. During each cycle, the system was operated in a total recycle mode, i.e., the permeate was recycled to the tank, thus keeping the concentration and volume of the suspension in the tank constant. In the second cycle, 100 L of whitewater was introduced in the tank while the same volume of filtrate was discharged. The same procedure was carried out in the third cycle. In the end of the treatment, five different effluents were characterized: raw whitewater (RW), ultrafiltered whitewater (UW), the first cycle concentrate (C1), the second cycle concentrate (C2) and the third cycle concentrate (C3). The physical and chemical parameters of each effluent were determined after the treatment according to the Standard Methods for the Examination of Water and Wastewater (AWWA, 1998).

2.2. Results and discussion

The characterization of the generated effluents after UF is presented in Table 1.
Ultrafiltration removed 44% of COD and 39% of BOD from the whitewater, showing that a considerable portion of the organic matter is particulated. The whitewater biodegradability (BOD/COD ratio) increased after UF from 45% to 50%, showing that part of the suspended solids are non-biodegradable. Suspended solids were completely removed by UF and a turbidity reduction of 99% was observed after treatment turning the filtrate very clear. As expected, dissolved solids were not removed by ultrafiltration.

Flux was measured during treatment, as presented in Figure 3. A final flux of 150 L.m\(^{-2}.h\)^{-1} was observed after the third cycle. Although it is not possible to determine an accurate flux average in this type of experiment, the flux behavior observed during the tests showed that this type of suspension did not present a rigorous fouling tendency.

![Figure 3 – Flux behavior during whitewater ultrafiltration](image)

According to the results it is possible to reuse the filtrates in the following areas of the paper machine such as water cleaning devices, low pressure showers, sealing waters, dilution water for paper additives. Each usage needs viability studies to avoid impacts on product or process caused by
conductivity, biological growing, pH and organic matter. These parameters must be controlled under the limits specified at a paper machine project or at a product specification.

The reuse of the filtrate in the bleach plant of an integrated mill would not be feasible specially because of the large amount of calcium ions which are the main cause of scale formation. So a method to remove these ions is presented in next section for a reliable use of whitewater on a bleaching process.

3. Calcium and magnesium removal from the whitewater

The method proposed to remove calcium and magnesium ions from the whitewater was based in the principle of precipitation followed by ultrafiltration. The precipitation of the ions was accomplished by bringing the pH of the suspension to 11. The reactions are showed as follow.

In Reaction 1, hydroxide ions are introduced into the system to react with bicarbonate ions giving carbonate ions and water molecules. The equilibrium constant of the reaction is also shown.

\[
\text{HCO}_3^{-} + \text{OH}^- \leftrightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \quad K_{eq} = \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^{-}] [\text{OH}^-]} = \frac{1}{1.8 \times 10^{-4}} \quad (1)
\]

Once carbonate ions are produced, Reaction 2 takes place in the system giving calcium carbonate precipitated salt, because of a low solubility equilibrium constant given at the experiment conditions.

\[
\text{CaCO}_3(s) \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-} \quad k_{ps} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = 1 \times 10^{-8} \quad (2)
\]

Calcium carbonate crystals are greater than membrane pore sizes, being removed by UF treatment. Whitewater is then characterized before and after treatment to evaluate efficiency.

3.1 Material and Methods

A UF membrane module with 170 cm² surface area was used. The type of membrane used in the treatment was the same as specified on topic 2.1.2. A peristaltic pump was connected to the module which operated in a 4 L-Becker. Air injection was made by a diffuser connected to a laboratory pump. The lab-scale membrane apparatus used in this test is presented in Figure 4.
Temperature of whitewater was kept in 50ºC according to industry real conditions. The pH was regulated to 11 by sodium hydroxide solution (1mol.L⁻¹) addition, to promote precipitation of calcium carbonate. This process was called “Low-hardness Ultrafiltration” (LhU).

3.2 Results and discussion

Hardness content in the whitewater, ultrafiltered whitewater and in the LhU filtrate as showed in Figure 5. About 94% of the whitewater hardness content was removed after LhU process application, against only a 27% removal after UF treatment. The final filtrate hardness achieved with this modified process was adequate to recycle the whitewater to the bleaching process, when compared with whitewater without treatment or with the ultrafiltered whitewater.

A total volume of 50 L of whitewater was treated by LhU process to further laboratory bleaching tests.
4. Whitewater reuse in the bleaching pulp process

4.1. Materials and Methods

4.1.1. Bleaching simulations

The whitewater, the ultrafiltered whitewater, the LhU filtrate and fresh water (reference) were used in laboratory bleaching simulations as process waters in the peroxide stage from the bleaching sequence $OD_0(\text{E}_{op})D_1P$. Figure 6 shows the layout of the bleaching sequence with the use of the whitewater as process water in the hydrogen peroxide stage. In each test, an industrial washed $D_1$ bleached pulp was used.

Figure 6 – Bleaching sequence layout

The conditions of the peroxide stage are showed in Table 2. The bleached pulp and filtrates were collected after bleaching simulations to further characterization.
4.1.2. Paper properties

The bleached pulp was refined in PFI refiner with fixed 50 degrees Schopper Riegler in the last refining stage. After refining, resistance and optical properties were measured in the four different pulps according to TAPPI Standard Methods (TAPPI, 1998).

4.2. Results and Discussion

4.2.1. Bleaching simulations

The four different waters from sub-item 4.1.1 used in the peroxide stage as process waters generated the respective filtrates and bleached pulps after stage simulation. Properties of pulp and filtrates are given respectively on Tables 3 and 4.

Pulp properties after bleaching, in general, were not affected by whitewater reuse in comparison with fresh water trials. Brightness and brightness reversion remained constant after peroxide stage, showing that the components recycled to bleaching, with or without ultrafiltration, did not influence those optical properties. Pulp viscosity showed low variations among the four treatments, and were considered with high enough for commercial purposes. Organochlorine compounds, on the other hand, increased considerably in bleached pulps from bleaching simulations with recycled whitewater. Further studies may identify the groups of compounds in whitewater that contribute to the raise of OX values after bleaching simulations.

The occurrence of scales and deposits in the bleach plant is only possible if calcium and magnesium free ions are present in water. Carbohydrates (cellulose and hemicelluloses) from the pulp may complex with those ions in the presence of hydroxyl groups at their chemical structure. The results showed that the pulp after D1 stage is saturated by ions of calcium and magnesium and whitewater or ultrafiltered whitewater reuse in peroxide stage affected considerably hardness content in process water.
Samples

Parameters | Pulp 1 (fresh water) | Pulp 2 (whitewater) | Pulp 3 (UF whitewater) | Pulp 4 (UF whitewater low hardness)
---|---|---|---|---
Brightness A.D.*, % ISO | 88,4 | 88,2 | 88,5 | 88,1
Brightness O.D.**, % ISO | 85,5 | 85,4 | 85,9 | 85,9
Brightness reversion | 2.87 | 2.81 | 2.66 | 2.15
Viscosity, dm³/kg | 854,2 | 863,9 | 832,2 | 843,0
OX, mg/kg | 92,4 | 177,6 | 197,5 | 175,4
Ca, mg/L | 220,5 | 261,1 | 234,8 | 215,5
Mg, mg/L | 40,7 | 40,7 | 43,1 | 47,7

* air dried
** oven dried

Peroxide stage filtrates quality varied significantly. The use of whitewater in bleaching caused an increase in filtrate conductivity and pH. Total dissolved solids in Filtrates 2, 3 and 4 was higher than the reference (Filtrate 1), showing that dissolved solids in the systems are due to the presence of free ions in aqueous phase, which may increase the corrosion potential in the system.

The hardness content in Filtrate 4 was very close to reference (Filtrate 1), showing that ultrafiltered whitewater with low hardness can be reused to bleaching process without formation of scale and deposits.

Copper and manganese ions did not present significant variation on filtrates and their presence was insignificant.

Table 4 – Characterization of filtrates after peroxide stage

| Parameters | Filtrate 1 (fresh water) | Filtrate 2 (whitewater) | Filtrate 3 (ultrafiltered whitewater) | Filtrate 4 (LhU whitewater)
---|---|---|---|---
pH | 8,30 | 8,52 | 8,78 | 9,82
Conductivity, µS/cm | 477 | 2040 | 1947 | 3080
TDS, mg/L | 615 | 2690 | 2581 | 4150
COD, mg/L | 339 | 462 | 444 | 384
Hardness, mg CaCO₃/L | 6,1 | 63,2 | 42,8 | 14,3
AOX, mg/L | 2,45 | 5,45 | 7,35 | 7,15
Cu, mg/L | ND* | ND* | ND* | ND*
Mn, mg/L | 0,04 | 0,06 | 0,05 | 0,01
Fe, mg/L | ND* | ND* | 0,02 | 0,34
Ca, mg/L | ND* | 9,5 | 6,4 | 2,0
Mg, mg/L | 0,7 | 5,6 | 3,9 | 0,9

*ND – non-detected

4.2.2. Paper properties

The most important mechanical and optical properties were evaluated on bleached pulps. No significant differences were found among the four bleached pulps as showed in Figure 7. The relationship between properties was the same according to the statistics test of identity on regression models. By this test the paper sheets of the four bleached pulps presented similar responses on laboratory standard tests. All properties were related to tensile index (TI), used as a reference property in the paper industry.
5. Conclusions

Whitewater ultrafiltration with polymeric membranes is technically feasible showing an excellent suspended solids removal and a non-rigorous fouling potential. The treated whitewater might be used in some paper machine processes such as water cleaning devices, low pressure showers, sealing waters, dilution water for paper additives.

Ultrafiltration per se was not enough to remove some contaminants, e.g., calcium ions, in order to enable the filtrate reuse in the pulp bleach plant of an integrated mill.
The removal of these ions was achieved with good results by ultrafiltration combined with chemical precipitation treatment, called Low-hardness Ultrafiltration (LhU). The system consists of the precipitation of calcium by elevating the pH and its removal by ultrafiltration.

The use of ultrafiltered paper machine whitewater with low hardness in bleach plant pulp washers in substitution of fresh water was technically feasible. Bleached pulp did not show significant differences on properties compared to fresh water. Filtrate conductivity, pH and TDS tended to increase after bleaching using whitewater, when compared with fresh water.

Mechanical and optical properties were not affected by whitewater recycle in bleaching, maintaining the final product quality.

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7. References


