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A NOVEL WAY OF COMBINING CHLORINE DIOXIDE AND MOLYBDATE CATALYZED HYDROGEN PEROXIDE FOR IMPROVED DELIGNIFICATION AND BLEACHING OF EUCALYPTUS KRAFT PULP

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Keywords: Chlorine dioxide, D_{hot}/P_{Mo} stage, hydrogen peroxide, molybdate catalyst, recycle process

ABSTRACT

The objective of this study was to evaluate different variations of the combination of a hot chlorine dioxide (D_{hot}) stage and an acidic molybdate catalyzed hydrogen peroxide stage (P_{Mo}), and to compare to other state-of-the-art options for a first bleaching stage after oxygen delignification and prior to an alkaline extraction stage. Laboratory bleaching trials were conducted with oxygen delignified eucalyptus kaft pulp samples provided by Brazilian pulp mills, with kappa numbers ranging between 10.0 and 12.9, and initial brightness values ranging between 50.0% and 56.5% ISO. Surprisingly and in contrast to previous scientific and patent literature, the D_{hot}/P_{Mo} process variant, i.e. a short hot chlorine dioxide stage followed without intermediate washing by an extended acidic molybdate catalyzed hydrogen peroxide stage turned out to be most effective with regard to kappa number reduction and brightness gain while causing only a moderate viscosity loss which is even smaller than observed in a single D_{hot} stage. It also allows a significant reduction of the chlorine dioxide charge in its D_{hot} part. Full bleaching sequences were run including the four-stage bleaching sequence D_{hot}/P_{Mo}-E_P-D_1-P and the three-stage bleaching sequence D_{hot}/P_{Mo}-E_P-D/P, which were compared to the conventional state-of-the-art four-stage bleaching sequence D_{hot}-E_P-D_1-P with respect to brightness gain, brightness stability, and chemical consumption. A recently developed economical recovery and recycle process for the molybdate catalyst is briefly introduced as well.

INTRODUCTION

The use of transition metal ions such as tungsten and molybdenum as catalysts for delignification and bleaching of lignocellulosic pulp with hydrogen peroxide under acidic conditions is described in the patent literature as early as 1984 by R. C. Eckert. In 2008 a paper was published by R. Agnemo *et al.* which provides detailed insight in the effectiveness and reaction mechanism of peroxomolybdate catalyzed pulp bleaching with hydrogen peroxide. J. L. Colodette *et al.* presented benefits and feasibility of a mill-scale P_{Mo} stage at the International Pulp Bleaching Conference in 2008. The first reference of the simultaneous use of chlorine dioxide and sodium molybdate catalyzed hydrogen peroxide for pulp delignification and bleaching at acidic pH is a patent application by T. Cho *et al.*, and dates back to 1995. S. Chaiarrekij *et al.* (2003) and R. C. Francis *et al.* (2006) investigated the partial replacement of chlorine dioxide by hydrogen peroxide catalyzed by sodium molybdate and identified possible reactions involved. In 2007 R. C. Francis *et al.* also suggested a recovery and recycle process for the molybdate catalyst which would make its commercial application more attractive. The objective of this study was to evaluate different variations of the combination of a hot chlorine dioxide (D_{hot}) stage and an acidic molybdate catalyzed hydrogen peroxide stage (P_{Mo}) and to compare to other state-of-the-art options for a first bleaching stage after oxygen delignification and prior to an alkaline extraction stage. An economical recovery and recycle process for the molybdate catalyst which was recently developed by T. Dietz *et al.* (2009) will be briefly introduced as well.

MATERIALS AND METHODS

Eucalyptus kraft pulp samples after oxygen delignification were provided by four different Brazilian pulp mills. Initial kappa numbers varied between 10.0 and 12.9, and the range of initial brightness values was between 50.0% and 56.5% ISO.

Bleaching and extraction stages under atmospheric pressure were carried out in double-sealed plastic bags immersed in temperature-controlled water baths. Interstage washing was simulated by diluting down to 2% consistency, filtering through a Buchner funnel and additional dewatering in a centrifuge. Extraction under oxygen pressure was carried out in a rotating autoclave at 0.3 MPa. Ozone treatment was conducted at room temperature with pulp well fluffed at 35% consistency.

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If not otherwise stated in the text or figures, in all trials throughout this study bleaching parameters were as follows:

- Consistency: 10%
- P_{Mo}: 90°C, 0.5% H_2O_2, 500 ppm molybdenum as $Na_2MoO_4 \bullet 2\ H_2O$
- D_{hot}: 90°C, kappa factor: 0.15
- Retention time in P_{Mo}, D_{hot} or combinations: 120 min, in D_{hot}/P_{Mo}: 15 + 105 min
- E_P: 60 min, 80°C, 0.4% H_2O_2, end pH: approx. 11
- D_1: 120 min, 80°C, 0.6% ClO_2 (as active chlorine), end pH: approx. 4
- P: 60 min, 80°C, 0.4% H_2O_2, end pH: approx. 10.5
- D_1/P: 10 + 90 min, 85°C, 0.2% ClO_2 (as active chlorine), end pH in D_1: approx. 5.5; 0.5% H_2O_2, end pH in P: approx. 10.5

Handsheets were prepared at pH 6 from 5 g of pulp on a Buchner funnel followed by drying and pressing under vacuum. Brightness was measured in % ISO following PAPTAC standard E.1 with Konika-Minolta spectrophotometer CM-3600d. Brightness reversion under humid conditions was determined as post color number according to PAPTAC standard E.4P (TAPPI T 260). Kappa number was measured according to TAPPI standard T 236 om-99, pulp viscosity in mPa•s according to TAPPI standard T 230 om-99, and chemical oxygen demand (COD) in kg/t according to DIN 38409.

RESULTS AND DISCUSSION

In a first study, the influence of temperature and catalyst concentration on delignification efficacy in a molybdate catalyzed hydrogen peroxide stage (P_{Mo}) was investigated. The P_{Mo} stages were run with eucalyptus kraft pulp having a kappa number of 10.3 with 1.0% H_2O_2 and an end pH between 3.5 and 3.8. The minimal kappa number of about 3 was achieved with 500 ppm molybdenum at 90°C, with 1000 ppm molybdenum at 80°C or with 1500 ppm molybdenum at 70°C for a retention time of 2 h. By extending retention time to 3 h, a final kappa number of close to 3 could be achieved even at 60°C with 2000 ppm molybdenum. Thus, a lower temperature can be compensated for by a higher catalyst concentration. Since 90°C was used in all first stages throughout this study, 500 ppm molybdenum was applied in molybdate catalyzed hydrogen peroxide stages for optimal delignification efficacy. In additional exploratory trials in which 1.0% H_2O_2 was applied, residual oxidant was found, when a D_{hot} stage and a P_{Mo} stage were combined as D_{hot}/P_{Mo} with 15 min D_{hot} followed by 120 min P_{Mo} without intermediate washing or as $D_{hot}+P_{Mo}$ with all chemicals combined from the beginning for 135 min, whereas no residual oxidant was found for the P_{Mo}/D_{hot} variant with 120 min P_{Mo} and subsequent 15 min D_{hot}. Despite a higher amount of residual oxidant, the highest values for brightness and the lowest values for kappa number were obtained for the D_{hot}/P_{Mo} variant compared to the other two variants. Consequently, hydrogen peroxide charge could be decreased to 0.5% without negatively affecting the delignification efficacy of D_{hot}/P_{Mo}. **Figure 1** shows the comparison of the three aforementioned process variants of combinations of D_{hot} and P_{Mo} with other state-of-the-art first bleaching stages, such as D_{hot}, ozone (Z), P_{Mo}, acid treatment (A) or hydrogen peroxide without catalyst at acidic pH (P_A).

The surprising finding that the D_{hot}/P_{Mo} process variant is most effective in delignification compared to the other possible variations was confirmed in this study. This is in contrast to previous patent and scientific literature. Since the difference between simultaneous and subsequent use of chlorine dioxide and hydrogen peroxide is not dramatic in our study (Figure 1), mutual decomposition reactions between these two chemicals under acidic conditions seem to play a minor role. These reactions could, however, be the explanation for the slightly lower efficacy of the simultaneous use of these chemicals. The slight superiority of the D_{hot}/P_{Mo} variant over the P_{Mo}/D_{hot} (105 + 15 min) variant could be explained with the rather short reaction time of chlorine dioxide. It is well known that delignification proceeds further in a D stage, even though chlorine dioxide is consumed very quickly. Of course, since the total amount of oxidation equivalents in our trials is higher for the combination stages compared to the single stages D_{hot} and P_{Mo}, it could be anticipated that a significantly lower kappa number can be achieved compared to the individual stages. On the other hand, it is highly questionable whether a kappa number as low as 1.4 can be reached with either single stage even by further increasing the oxidant concentration. There are hints in the literature that the reduction of the kappa number in a P_{Mo} stage is a consequence of the removal of both lignin and hexenuronic acid (HexA). J. Jäkärä *et al.* concluded in a publication in 1999

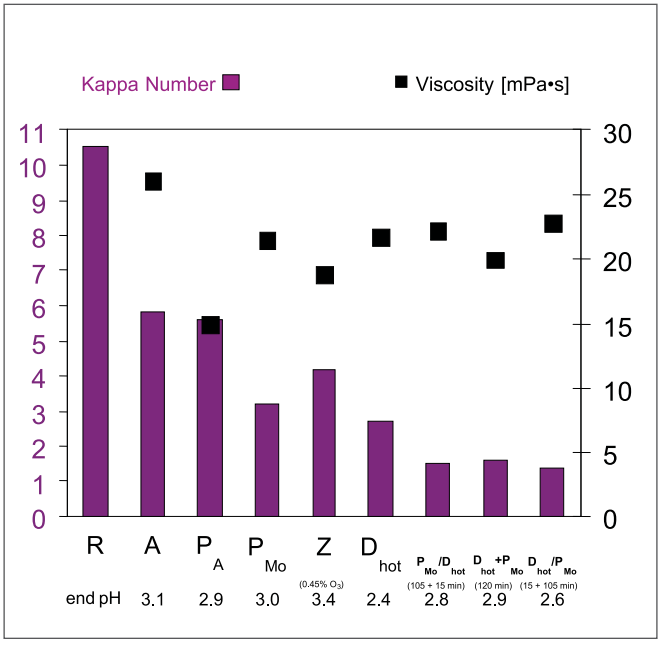

Figure 1. Kappa number and viscosity after a subsequent EP stage for different first stages. The eucalyptus kraft pulp sample had an initial kappa number of 10.5 (R)

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that molybdate catalyzed hydrogen peroxide preferentially attacks HexA, and then lignin, whereas the pathway for chlorine dioxide is the opposite. Hence, chlorine dioxide and molybdate catalyzed hydrogen peroxide complement each other in their modes of action, which makes it even more sensible to combine the two in one stage. Regarding viscosity, it is interesting to note that the drop in viscosity for the combination stage is comparable to the individual stages. Summarizing the results in Figure 1, the delignification efficacy of various first stages under the given conditions can be put in the following order: $D_{hot}/P_{Mo} > D_{hot} > P_{Mo} > Z > A$. In an acidic peroxide stage without catalyst (P_A), the degree of delignification is similar to a sole acidic stage, but the presence of hydroxyl radicals generated from hydrogen peroxide results in a significant decrease in viscosity. Even though brightness gain in this early stage of the bleaching sequence is less important than kappa number reduction, it should be mentioned here that in the same study the highest brightness and the lowest color reversion was also obtained for the D_{hot}/P_{Mo} variant.

Since it is well known that the pH is a crucial parameter for delignification and bleaching effectiveness, a systematic study was conducted on the influence of pH on the performance of P_{Mo}, D_{hot} and combinations thereof. The same pulp sample was used as in the study of Figure 1 and the results are shown in **Figure 2**. For both a single P_{Mo} and a single D_{hot} stage, a lower end pH results in a lower kappa number for the same chemical charge.

The same seems to be valid for the combination stage D_{hot}/P_{Mo}. For a single D_{hot} stage, a significant increase of the kappa factor from 0.15 via 0.2 to 0.25 at the same pH level of 2.4 – 2.6 does not result in a significant further decrease of the kappa number. It can also be derived from the graph in Figure 2 that the kappa factor in a D_{hot}/P_{Mo} stage can be reduced even down to 0.075, and yet the resulting kappa number is still lower than in a single D_{hot} stage with a kappa factor of 0.25. This is remarkable, since in this case the total amount of oxidation equivalents is significantly lower in the combination stage compared to the single D_{hot} stage. There are some trends for the relationship between end pH and viscosity drop, but these minor differences are not of practical relevance.

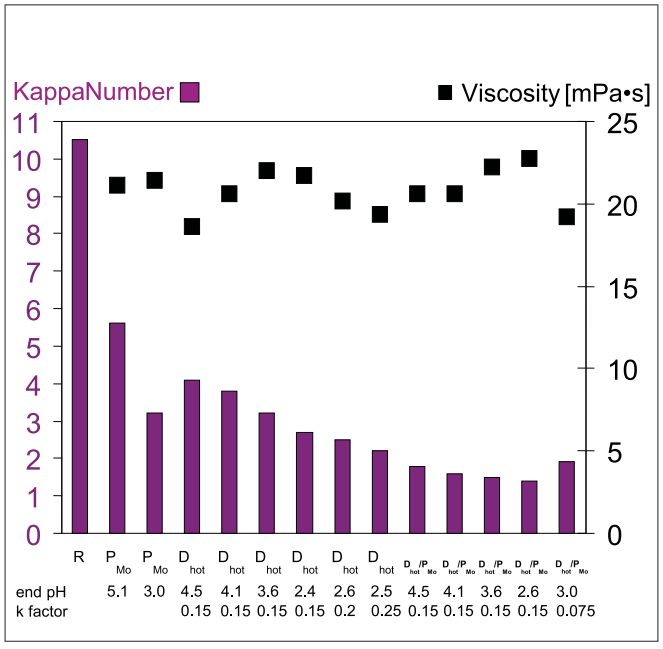

Figure 2. Kappa number and viscosity after a subsequent E_P stage for P_{Mo}, D_{hot} and D_{hot}/P_{Mo} at different pH values and for different kappa factors in D_{hot}. The eucalyptus kraft pulp sample had an initial kappa number of 10.5 (R)

As a next step in this study, we ran full bleaching sequences comparing the D_{hot}/P_{Mo} combination with D_{hot} as the state-of-the-art first stage. In one series, kraft pulp having an initial kappa number of 10.3 and an initial brightness of 52.3% ISO was bleached with a D_{hot}/P_{Mo}-E_P-D_1-P sequence at different catalyst temperature combinations in comparison to a D_{hot}-E_P-D_1-P sequence. The results allow to expand the conclusion from our earlier finding, that a lower temperature in the P_{Mo} stage can be compensated by a higher catalyst concentration to the D_{hot}/P_{Mo} combination, as well as to a full bleaching sequence. Only with 60°C and 2000 ppm molybdenum in the D_{hot}/P_{Mo} stage was the final brightness target of 90 ± 0.5% ISO missed, though only slightly. It is important to stress the fact that the kappa factor was only 0.15 in the combination stages compared to 0.2 in the single D_{hot} stage, and yet the same or even higher brightness could be achieved. There was, however, a clear trend noticeable for the development of brightness and brightness stability with decreasing temperature. Thus, for maximum brightness and brightness stability, a temperature of 90°C is highly recommended for both a D_{hot} and a D_{hot}/P_{Mo} stage. The superiority of the D_{hot}/P_{Mo} variant over the other two possible combinations, i.e. $D_{hot}+P_{Mo}$ and P_{Mo}/D_{hot}, could be confirmed in another study, in which kraft pulp was fully bleached in a three-stage bleaching sequence starting with either D_{hot} or a combination stage and followed by -E_P-D_1/P. Again, a kappa factor of only 0.15 was applied for the combination stages, whereas a kappa factor of 0.2 was applied for the single D_{hot} stage. The brightness target of 90 ± 0.5% ISO was clearly missed in case of the P_{Mo}/D_{hot} variant, but was met in all other cases. The highest brightness stability (post color number of 0.221) was achieved with the D_{hot}/P_{Mo} combination, followed by $D_{hot}+P_{Mo}$ (0.241), P_{Mo}/D_{hot} (0.531) and D_{hot} (0.625). This study also showed that it is possible to reduce the number of bleaching stages to only three. By leaving out the intermediate washing step, the final D and P bleaching stages are combined to one stage. Only the pH change from acidic to alkaline is still required for the activation of hydrogen peroxide.

In order to specify the potential cost savings by substituting a D_{hot}/P_{Mo} combination for a D_{hot} stage in a full bleaching sequence, kraft pulp with an initial kappa number of 10.3 and an initial brightness of 55.1% ISO was bleached with either a D_{hot}/P_{Mo}-E_P-D_1-P or a D_{hot}-E_P-D_1-P sequence.

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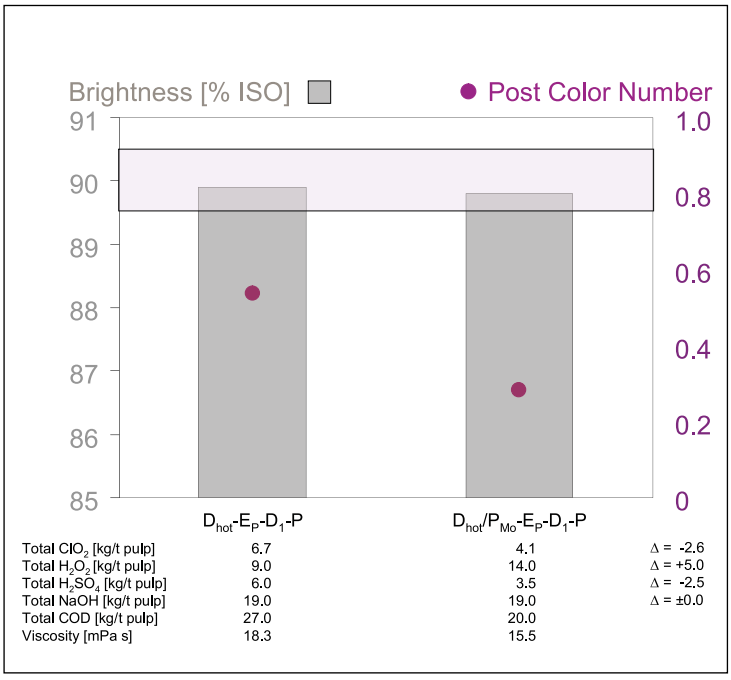

Total ClO_2 [kg/t pulp]	6.7	4.1	Δ = -2.6
Total H_2O_2 [kg/t pulp]	9.0	14.0	Δ = +5.0
Total H_2SO_4 [kg/t pulp]	6.0	3.5	Δ = -2.5
Total NaOH [kg/t pulp]	19.0	19.0	Δ = ±0.0
Total COD [kg/t pulp]	27.0	20.0	
Viscosity [mPa s]	18.3	15.5	

Figure 3. Brightness, brightness stability as post color number, total chemical charges, total COD and viscosity of pulp fully bleached with a D_{hot}/P_{Mo}-E_P-D_1-P or a D_{hot}-E_P-D_1-P sequence. The eucalyptus kraft pulp sample had an initial kappa number of 10.3 and an initial brightness of 55.1% ISO

	A	B	C	D
Total ClO_2 [kg/t pulp]	8.0	7.2	8.0	7.2
Total H_2O_2 [kg/t pulp]	13.0	13.0	13.0	13.0
Total H_2SO_4 [kg/t pulp]	12.0	11.0	5.5	9.0
Total NaOH [kg/t pulp]	18.0	18.0	18.0	18.0
Total COD [kg/ t pulp]	36.7	28.0	25.0	30.3
Viscosity [mPa s]	16.9	17.0	13.5	19.8

Figure 4. Brightness, brightness stability as post color number, total chemical charges, total COD and viscosity of pulp samples from four different Brazilian pulp mills fully bleached with a D_{hot}/P_{Mo}-E_P-D_1-P sequence. Initial kappa numbers and initial brightness values of the eucalyptus kraft pulp samples were as follows: A: 12.7, 50.0% ISO; B: 10.5, 56.5% ISO; C: 10.3, 52.3% ISO; D: 11.3, 55.8% ISO

Figure 3 shows the final brightness and brightness stability and, in addition, the total chemical charges, the total COD and the viscosity of the fully bleached pulp.

The final brightness target of 90 ± 0.5% ISO could be achieved in either case. For the D_{hot}/P_{Mo} sequence 2.6 kg/t less chlorine dioxide (corresponding to 6.8 kg/t as active chlorine), 2.5 kg/t less sulphuric acid and 5 kg/t more hydrogen peroxide were needed as compared to the D_{hot} sequence. Also, a significantly lower COD load was measured for the D_{hot}/P_{Mo} sequence. The slightly lower viscosity found for D_{hot}/P_{Mo} should not be of practical relevance. There is, however, a great advantage with regard to brightness stability: post color number for D_{hot}/P_{Mo} is only 0.283, whereas it is 0.537 for D_{hot}.

Finally, we wanted to investigate how differently pulp samples from different pulp mills respond to a D_{hot}/P_{Mo}-E_P-D_1-P sequence. The results are shown in **Figure 4**. In a first step of this study the same bleaching parameters were applied to all samples and in a second step, if the brightness target of 90 ± 0.5% was clearly overachieved, the chlorine dioxide charge in the D_1 stage was reduced to a level with which the brightness target could be still achieved. The chemical charges given in Figure 4 represent these optimized amounts.

It can be concluded that pulp sample A showed the poorest bleachability, whereas pulp sample B was the easiest to bleach. There were also found significant differences with regard to brightness stability, total COD and final pulp viscosity.

To our knowledge, the broad introduction of a P_{Mo} stage to the pulp & paper industry has failed, so far, mainly due to the lack of a recovery and recycle process for the molybdate catalyst. Recently, we developed such an economical process whose basic principle is very similar to the one suggested by R. C. Francis *et al.* (2007). Both are based on the fact that discrete molybdate anions are present under alkaline conditions, whereas heptamolybdate cluster anions are generated under acidic conditions. It is only the heptamolybdate anion which either forms an insoluble complex with cationic surfactants or is adsorbed to the surface of a cationically-modified bentonite. Dietz *et al.* (2009) suggested a simple process scheme in which the molybdate containing filtrate is passed through a modified filter pad retaining the molybdate, which is then flushed off with alkaline solution to obtain a concentrated molybdate solution which can be reused for the P_{Mo} stage (**Figure 5**). Proof of principle of this process has been given on lab scale so far, and is under development for scaling up at the moment. Implementation of an economical recovery and recycle process integrated into a bleach plant would make a P_{Mo} containing bleaching sequence a viable candidate for existing or future bleaching lines.

CONCLUSIONS

In contrast to previous scientific and patent literature, the D_{hot}/P_{Mo} process variant was found to be superior to the other two possible variants, i.e. D_{hot}+P_{Mo} and P_{Mo}/D_{hot}, and outperforms various other state-of-the-art options for a first bleaching stage after oxygen delignification with regard to kappa number reduction and brightness gain. This could

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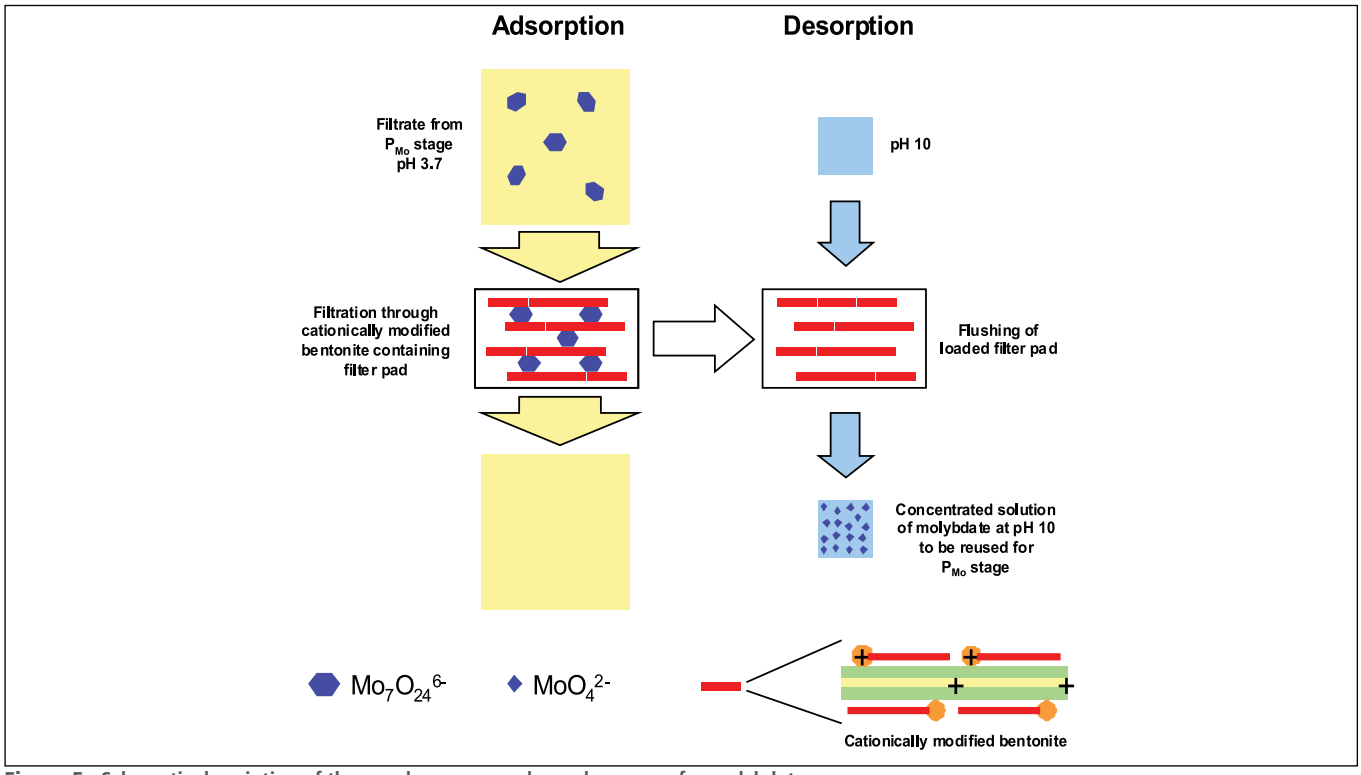

Figure 5. Schematic description of the novel recovery and recycle process for molybdate

be confirmed in several cases. The advantage is also carried through a full bleaching sequence. Whether a three-stage D_{hot}/P_{Mo}-E_P-D_1/P is sufficient or a four-stage bleaching sequence D_{hot}/P_{Mo}-E_P-D_1-P is required to achieve the brightness target of 90 ± 0.5% ISO depends on the bleachability of the individual pulp. Most important benefits of the combination stage are improved brightness stability and a significant reduction of the chlorine dioxide charge. This, in turn, allows either cost savings or an increase in production capacity, if chlorine dioxide generation is a bottleneck of a bleach plant. Optimal parameters for the D_{hot}/P_{Mo} stage are a temperature of 90°C, 15 min retention time for D_{hot} followed by 105 min for P_{Mo}, 500 ppm molybdenum concentration and a final pH of about 3. A lower temperature than 90°C can be compensated by a higher catalyst concentration, but for optimal brightness gain and best brightness stability, 90°C is most beneficial. It should be possible to easily implement a D_{hot}/P_{Mo} stage in an existing bleach plant by injecting chlorine dioxide into an MC pump prior to an up-flow tube followed by addition of hydrogen peroxide and sodium molybdate on top of the down-flow bleaching tower. With an economical recovery and recycle process for the molybdate catalyst in place, a D_{hot}/P_{Mo} stage would become an attractive alternative to the conventional D_{hot} stage. ■

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