New trends for evaluation of washing efficiency –Based on chemical oxygen demand

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ABSTRACT

The efficiency of pulp washing at present is being measured as the loss of sodium sulfate per ton of pulp and other losses are being ignored. Easily washable sodium is of very doubtful value as a measure of washing loss for kraft pulps, since all washable sodium can be washed out if enough water is used. Environmental effects can not be predicted simply from the inorganic washing loss of the pulp.

Now as the environmental implication of the pulp industry have been widely recognised, washing standards tend to be set by pollution abatement consideration.

By reducing the chemical oxygen demand in pulp by washing a lot of organic load can be reduced in the effluent which will in turn save the cost of treatment. Secondly it reduces the consumption of bleaching chemicals, chemical oxygen demand in bleach plant effluent and quantities of organic halogens which are highly toxic.

In the present paper an attempt is made to show the difference between washing of the organics (mainly lignin) and inorganics (mainly sodium.) The effect of poor washing of organics compounds on bleach plant effluent is also reviewed. The stress has been given on determining washing efficiency in term of chemical oxygen demand (COD) instead of soda loss as sodium sulfate. A relation between soda loss and chemical oxygen demand in washed pulp is also developed.

INTRODUCTION

After cooking of chemical pulps, the spent cooking liquor in the pulp contains dissolved organic and inorganic substances, the quantity of which can be quite considerable. The dissolved substances may cause serious water pullution if they are not taken care of and destroyed. Furthermore, organic substances are of considerable heating value if recovered and burnt for steam production. The inorganic chemicals are also of great value as raw material for the preparation of new cooking liquor. In sulfate pulping process at least 200 to 400 kgs. of cooking chemicals per ton of pulp are used which are changed into corresponding lignin compounds. Thus in order to clean the pulp to make it suitable for further processing and to bring down the production cost, it is essential to remove and recover these substances from spent liquor. With this aim, the washing of pulp was started in year 1818 by kraft industries.

Countercurrent washing on a battery of rotary drum vacuum filters is presently the standard practice for pulp washing. As a general rule, the more wash water used, the greater is recovery of chemicals. However, later this water must be evaporated which consumes high amount of steam energy and thus the objective of washing is to deliver the black liquor to

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the recovery plant having as high concentration of solids as possible and at the same time to deliver the stock to the screen room substantially free of soda and other dissolved solids. The performance of washing has great influence on the economics of entire mill. Therefore, the washing plant must be optimally operated.

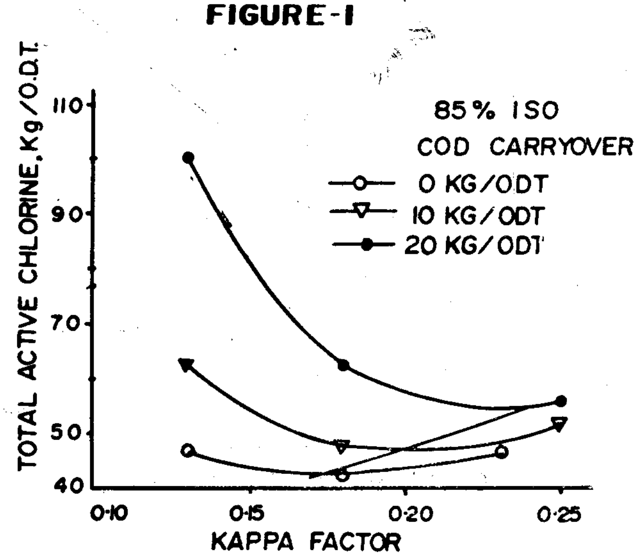
To obtain a measurement of the efficiency of the washing operation in a sulfate or soda pulp mill, the sodium content in the pulp leaving the washing stage is usually determined, and the result is expressed in for instance, kg Na_2SO_4/ton pulp. The other losses are ignored. Expressing washing efficiency as soda loss in terms of salt cake originates from the fact that salt cake is used as make-up chemicals in the sulfate mill. For accounting purposes it is easier to express the loss in terms of what must be purchased. When economy was the main criteria and environmen'al pollution was not playing an important roll, the washing efficiency in terms of soda loss was relevant But now, when the environmental implications of the pulp industry become widely recognised, washing standards tended to be set by pollution abatement considerations. The new standard required new indicators-lignin, BOD/COD, color etc. for calculation and measurement of washing efficiency.

WASHING LOSS AND THE ENVIRONMENT :

It is obvious that any residual spent liquor leaving the washing operation with the pulp will be washed out in a subsequent, open process stage (e g. the screening or bleaching) and contributes to the water pollution and will be source of BOD, COD and color and will also interfere with the bleaching of pulp. It has been reported by Pant et al (7) that original black l quor contains three major components, namely inorganic component about 23-29%, lignin about 35-46% and remaining portion contains mostly organic acids derived from lignin and carbohydrate degradation. They have also reported that 50% of COD value and 90% of the color in black liquor is due to lignin. So, during the washing the removal of organics, mainly lignin is very much important for reducing the pollution.

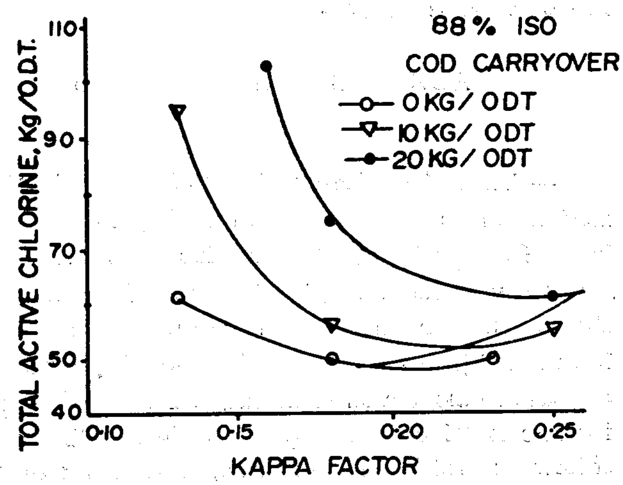
It has been reported by Lindstrom and Norden (8) that dissolved organic material (COD), remaining in the pulp after washing increases bleach chemical consumption. The optimum charge of active chlorine in first stage in significantly increased (Fig 1 & 2). Dissolved organic material carried over from washing will be further degraded in the chlorination stage. It has been indicated that the degradation/oxidation of the carryover is dependent on kappa factor (charge of active chlorine as % of pulp divided by the kappa number of well washed pulp). Although this degradation

FIGURE-I



Influence of carry over on total active chlorine consumption (8:% ISO,) Kappa no. 17.7).

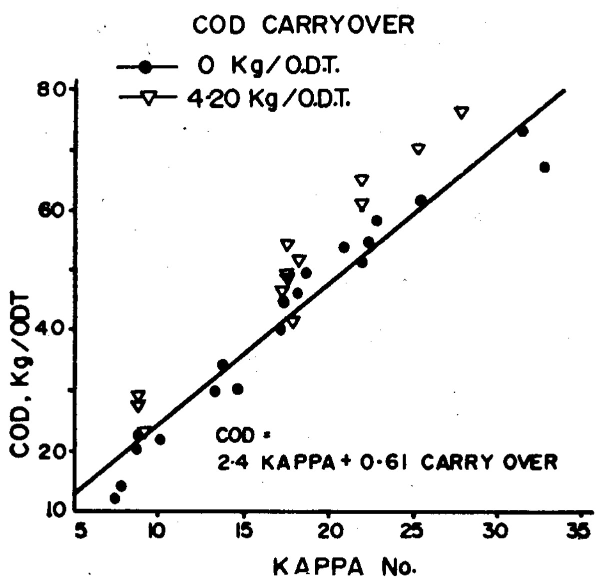
FIGURE-2



Influence of carry over on total active chlorine consumption (88% ISO, Kappa no. 17. 7).

will decrease the original COD value of this carry over, it will still add to the total effluent COD value. About 60% of the dissolved organic material carried in to the chlorination stage adds to the total effluent COD value (Fig 3).

FIGURE-3



COD in effluents from bleaching,

AOx Formation

AOx is the generic term for adsorbable organic halogens. Here, it refers to chloro-organic material dissolved in spent bleach liquors, which can be absorbed on activated carbon. AOX formation ia related to the use of chlorine and chlorine dioxide in the chlorination stage as under—

$$AOX = 0.086*Cl_2+0.12*ClO_2/5$$

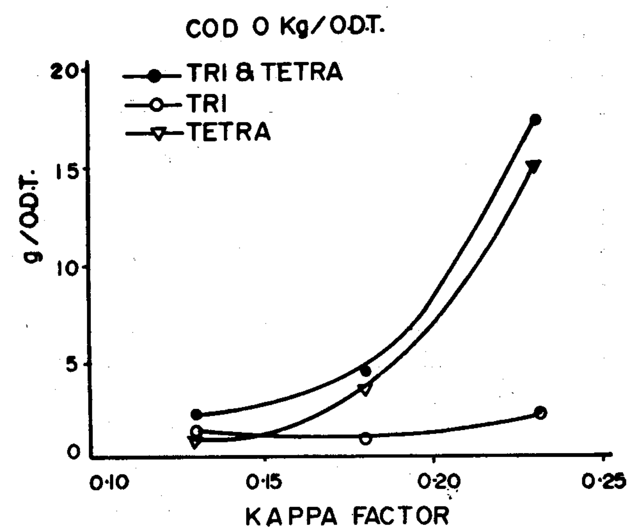
— Thus, the influence of wash loss on AOX formation can be estimated, considering that optimum kappa factor is increased with increased wash loss. This has been reported (8) that even if the degree of chlorine dioxide substitution in the first stage is as large as 50%, dissolved organic materials carried with the pulp to the bleach plant might, if washing is poor, increase AOX discharge by more than 40%. If only chlorine is used in the first stage, the amount of AOX formation will be much more.

Chloro-phenolic compounds

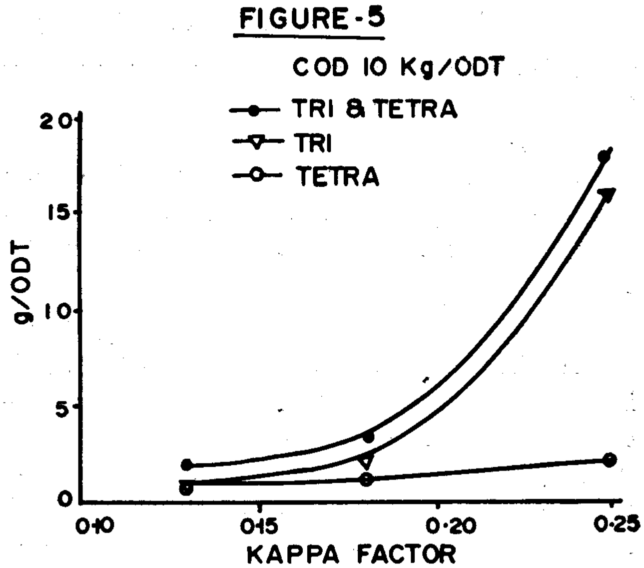
Chlorinated phenols are known as highly toxic compounds to aquatic life. Chloroguaiacols have been shown to bio-concentrate in the fish. The bio-accumlation potential increases with increasing numbers of Cl-atoms in the atomic ring. Chloro-phenolic compounds discharged from bleach plant can be methylated by bacteria present in the sediment and turned in to chlorinated anisols and veratrols. This group of compounds is more toxic and potentially more bio-accumlative than original chloro-phenolic compounds.

It has been reported by Axegard (9) that the formation of these compounds is almost exponentially related to the kappa frctor. Norden's etal has given graph of amount of 6, 7 & 8 tri & tetra-chlorophenol vs kappa factor (in the (C50+D50) stage) at wash losses corresponding to o, 10 & 20 kg COD per od ton (Fig 4, 5 & 6.) At first glance the results may seem puz zling. When compring at a given kappa factor, a higher COD carry over resulted in decreased formation of tri & tetra chlorophenolic compounds. However, when considering the effect of wash loss on optimum kappa fnctor which is much higher at high COD loss (Table No. 1),the net result will increase the formation of these compounds. Thus poor washing has even worse effects on formation of these compounds than on total organically bound chlorine. Chlorinated dioxins/furans also increases with poor washing (Fig 7&8).

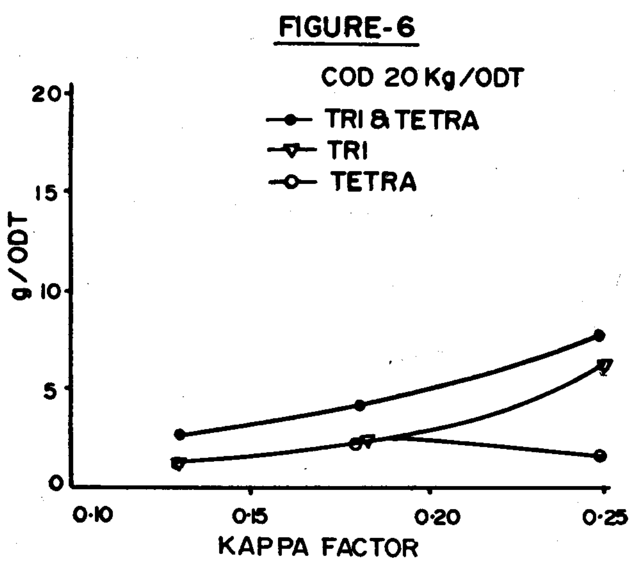
FIGURE-4



Plot of tri-and tetra-chlorophenolic compounds, at zero wash loss.



Plot of tri-and tetra-chlorophenolic compounds, at 20 kg. COD/o.d.t. wash loos.



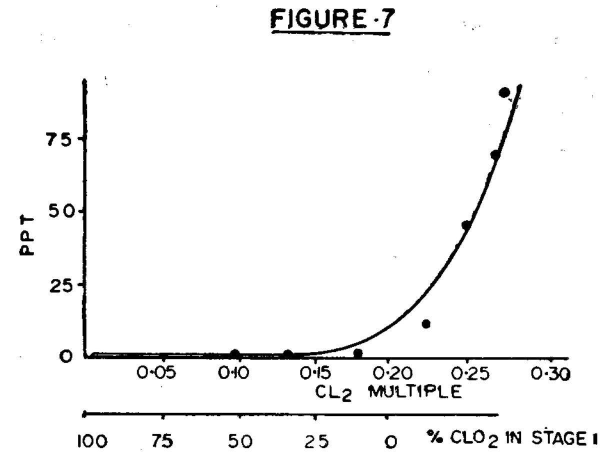
Plot of tri-and tetra-chlorophenolic compounds, at 20 kg COD/o.d.t. wash loss.

Table No. 1

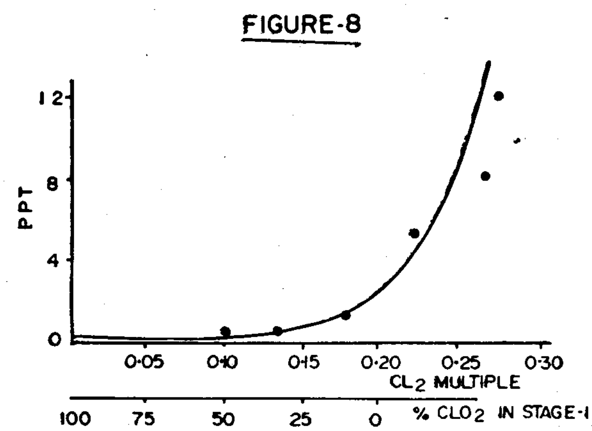
Optimum Kappa Factors

(C50+D50) (ED) D; Kappa No. 17.7

COD Kg/o d.t.	Kappa Factor 85% ISO	88% ISO
20	0.24	>0 25
10	0 20	0.23
0	0.17	0.19



Amount of 2,3,7,8-TCDD in bleached pulps ves the Cl_2 multiple.



Amount of 2,3,7,8-TCDF in bleached pulps vs the Cl_2 multiple.

Thus, the importance of removing dissolved organic materials prior to bleaching is obvious. Through washing is important to minimize bleach chemical consumption and discharged of chlorophenolic compounds from bleach plant.

WASHING-ORGANIC VS INORGANIC COMPOUNDS

Literature Review

Grahs (19) has reported that when the washing losses are high, exceeding 15 to 20 kg sodium sulfate per ton pulp, a fair correlation exists between the sodium content and the content of organic substances in the filtrate from the pulp suspension. From the sodium content it is possible to calculate the amount of organic substances. Thus the BOD/COD can also be deduced in the pulp.

When, however, an upto date washing plant is used and the washing losses are very low, there is no fair correlation between the sodium content and the value of BOD/COD. This depends on phenomenon such as, for instance, adsorption which influence the washing operation and its a well known fact that diff erent substances have different adsorption isotherms.

It is further reported that adsorption of lignin on pulp fibre is considerably lower than sodium ions. However, lignin has much slower mass transport rate between flowing and stagnant liquors compared to sodium ions. Because lignin molecules are large in comparison to sodium ions and thus lignin molecules are unable to reach all parts of flowing liquor and have lower mass transfer coefficient. The lignin molecules may be trapped or nearly trapped to a great extent than sodium ions. This, consequently, will cause a slower mass transport for lignin molecules than for sodium ions. He then concluded that due to this difference in rates of adsorption on the pulp and mass transport time the mass part of the lignin is most easily washed out in comparison with the sodium ions. The last part of the lignin takes more time to be washed out than the last part of the sodium.

Goring etal (18) reported the removal of lignin during the washing of pulp fibers by quantitative ultraviolet microscopy complemented by spectrophotometric exemination of the washed filtrate. Good agreement was showened between the results obtained by the two different methods. They reported that during pulp washing initially there is rapid removal of lignin followed by much slower removal which appears to be diffusion controlled.

Laxen (3) found that the concentration of dissolved organic matter decreases with decreasing sodium concentration in both pulp and wash filtrate during the washing procedure under mill conditions. In a filter line there is a linear correlation between TOC and sodium concentration, but liquor squeezed from a pulp mat has TOC concentration a little higher than the corresponding washing filtrate.

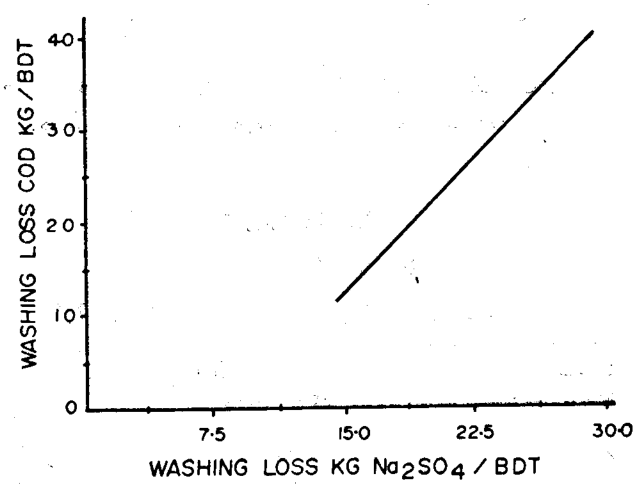
Similarly, during the study of washing after oxygen bleaching in a pilot plant, Jamiesson and Smedman (20) found that organic solids were washed out less effectively than inorganic solids. They concluded that calculations for pollution control and washing efficiency ought to be based on a lower efficiency value than calculation for salt cake loss.

Edward etal (1) made a computer simulation of the same pilot plant and reported that in the last washing stage, the efficiencies were not same for all components.

Hartler & 'Rydin (6) concluded that "easily washable sodium" which is used for designing new equipment, or in evaluating the financial aspects of increasing the capacities of the existing system, is of very doubt ful value as a measure of the washing loss/efficiency of Kraft-mill, since all washable sodium could be washed out if enough water used for washing. Thus the environmental effects can not be predicted simply from the inorganic washing loss of the pulps.

Tumoi (11) has given relationship between COD Kg/ADT and washing loss as sodium sulphate Kg/ADT which is a straight line (Fig. 9). He has also reported that it has been proven that the washing results given as COD Kg/ADT in relationship to sodium sulphate Kg/ADT highly depends upon the type of pulp, washing equipment, diffusion time, washing loss level etc.

FIGURE-9



Comparison between washing loss as Na_2So_4 in relationship to COD (in one case), from literature.

Experimental Work :—

Laboratory work is performed for finding out relationship between soda loss as sodium sulfate and chemical oxygen demand. For the purpose the second stage and third stage washed pulp samples are taken from a paper industry. The second stage washed pulp is divided into number of parts and then these samples are washed with varying amount of water and loading. These washed pulp samples and third stage washed pulp are finally analysed for Sodium and chemical oxygen demand. The results are given in table No. 2.

Table No. 2

Sodium as Sodium Sulfate vs Dissolved Organic Compounds (COD) leaving with the washed pulp

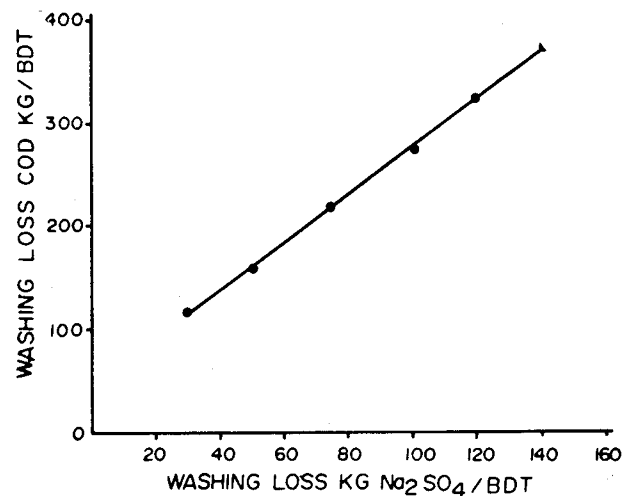
S.No.	Parameters (Kg/ODT Pulp) Soda Loss as Sodium Sulfat	Chemical Oxygen Demand (COD)
1.	141.15	371.08
2.	119.98	321.76
3.	100.89	272.27
4.	74.87	218.16
5.	50.13	158.26
6.	29.26	116.04

The chemical oxygen demand values are plotted against sodium sulfate which give a straight line (Fig. 10). From the graph it is clear that for higher concentrations there exist a relationship between COD and soda loss in the washed pulp and ratio of COD to soda loss is always more than one. It means that dissolved organic loss are higher than inorganic loss.

As reported by Bethge and Radestrom (16) the following points are kept in mind while analysing the COD in pulp samples—

1. Pulp suspension must be disintegrated for making a homogeneous sample.
2. To avoid the low COD value, it is useful to wash the pulp sample with weak sodium hydroxide solution.
3. A large number of washing results in a rather dilute filtrate.

FIGURE - 10



Comparison between washing loss as Na_2So_4 in relationship to COD (in one case), as per the present study.

It is recommended that the number of washings shall not be more than three.

In this study COD values are determined by the method mentioned in the 'standard methods for examination of water & waste water'; APHA-AWWA-WPCF (N.Y.) and soda loss by SCAN-test standard C-30.

Thus it is clear that washing efficiency of organic and inorganic compounds are not same and it is more difficult to remove organic compounds (mainly Lignin) than inorganic compounds (mainly Sodium). These organic compounds contribute to highly toxic compounds and thus cause more severe pollution problem.

SODIUM VS CHEMICAL OXYGEN DEMAND (COD):—

From the research work mentioned earlier it is clear that the parameter "washing losses/efficiency", bassed on sodium determination, had to be reevaluated. As an environmental parmeter it could not be considered relevant for determining washing efficiency. It is felt that the same parameter which is used for determining discharges shall also be used for knowing the washing loss. The parameter which represent the organic load in the effluent shall be considered for washing efficiency. The parameter which measure the organic load are total organic carbon (TOC), dissolved organic carbon (DOC), tolal oxygen demand (TOD), chemical oxygen demand (COD) and biological oxygen demand (BOD). The analysis of the parameters like TOC, DOC and TOD involves rigorous methods. Expensive apparatus are also required. Moreover, these parameters are not recognised as environmental discharged control. BOD and COD have been recognised as control parameters. When we see the practical aspect we find that it is simpler to determine COD value of the effluent than BOD as the procedure to determine the later parameter is tedious and time consuming

Therefore we should move over to use COD value as washing loss instead of sodium sulfate per ton of pulp. This is already being practiced in advanced countries like Sweden.

CONCLUSION :

As the Environmental Protection Regulations are being made more strict day by day, the future system design of washing shall be based on environmental aspecst rather than only overall cost profitability.

As from literature review and experimental work, it is clear that washing efficiency of dissolved organic compounds (COD) is poor than inorganic compounds and for higher soda losses, a relationship can be drawn between washing efficiency as sodium sulfate and dissolved organic compounds (COD) leaving with the pulp Moreover, these dissolved compounds left in the washed pulp create severe poliution problum due to formation of highly toxic chlorinated organic compounds.

Thus in future choice of washer, number of washing stages and operational parameters should be optimised to also remove more and more dissolved organic compounds (COD) and washing arrangement in future should be more efficient than we are so for used to. The washing efficiency must be given as dissolved organic compounds (COD) per ton od pulp. This will further increase the significance of Brown Stock Washing as one of the most important loops in the total process and will lead to efforts to develep even more efficient Brown Stock Washing models.

A more research work is needed to get relationship between washing efficiency of sodium expressed as sodium sulfate and dissolved organic compounds(COD) for different conditions such as type of raw material, washing equipment and kappa number etc.

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