



Sulphate Chemical Pulping (Anthraquinone) of *Morus nigra*

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ABSTRACT: The maximum tonnage for bleachable grade of pulp is produced today by sulphate chemical process all over the world as compare to other pulp manufacturing processes, because of some distinct superiority over other processes, in India sulphate chemical process is predominantly employed³, because of high pulp strength, versatility of pulping different raw materials, versatility of producing a wide range of pulp, efficient chemicals and heat recovery and reduced pitch troubles with resinuous woods. Use of Anthraquinone (AQ) in pulping has been found to have a marked catalytic effect. In addition to enhancing the rate of delignification, AQ is said to stabilize. For carbohydrates and at comparable permagnate numbers, unbleached pulp yields were always found to be higher for kraft AQ or soda AQ pulps, with no seemingly adverse effect on strength properties of bleached and unbleached pulp.

Keywords: Sulphate Chemical Pulping; Anthraquinone Mono Sulphate; *Morus nigra*; Kappa number; Pulp yield.

INTRODUCTION: To improve upon the soda process which suffers from low pulp yield of inferior quality^{1 & 3} caused by excessively long cooking time, higher temperature and caustic charges necessary to produce bleachable grade pulps, an additive was developed by Bach and Fiehn². They reported that by addition of small quantity of anthraquinone mono sulphate (AMS) as an additive to soda and kraft cooks of *Pine*, pulp was increased without any adverse effect on strength. AMS was found to stabilize polysaccharide towards alkaline degradation and to interact with lignin causing its rapid and extensive removal. However, AMS cost-benefit relationship constituted a barrier to its commercialization. Recently, Halton^{5 & 6} found that anthraquinone (AQ) and its derivatives with alkyl substituents (e.g. 2-methyl AQ) are superior additive to its sulphonate derivative AMS. Halton has called AQ as a miracle cures all additive in improving convention kraft pulping⁶. A flurry of trials in kraft⁷ and soda mills⁸ all over the world has been carried out after Halton's announcement in 1977. In India also, few efforts have been made to study the effects of AQ in pulping bamboo⁹, mixed hardwoods¹⁰ and softwood³.

Bach and Fiehn¹⁰ studied the stabilizing effect of AQ and other AQ derivatives in alkaline treatment of wood and found that 2-Na-anthraquinone monosulphonate was superior to others in preventing

carbohydrate degradation and solubilisation. Nomura¹¹⁻¹³ investigated the use of AQ and its derivatives as additives in various pulping processes. He found that they were effective in increasing the delignification rate, pulp yield and pulp quality. He postulated that stabilization of carbohydrates during cooking was responsible for the observed increase in pulp yield. With respect to lignin, he proposed that AQ facilitates β -ether cleavage producing lower molecular weight lignin fragments, thereby increasing the delignification rate. This lower molecular weight lignin fragment must explain the better bleachability of AQ pulps. Because a small amount of quinone was affected, he presumed that the additive was continuously regenerate through redox reaction.

The sulphate chemical process differs from the soda process by the presence of a certain amount of sodium sulphide, the sulphur of which is lost for the most part during cooking and subsequent treatment of the spent liquor. The name is derived from the custom of restoring the sulphur by the addition of sodium sulphate to the black liquor previous to incineration, sodium sulphide being formed by reduction. A modification of it is the soda-sulphur process, wherein sulphur is added directly, to the caustic soda liquor. During cooking some sodium thiosulphate is formed in addition to sodium sulphide. The pulps obtained by the sulphate

process and their modifications are essentially identical.

Goyal et al.¹⁴, Rajan et al.¹⁵, Blain¹⁶ and Dutta and Biermann¹⁷ have proposed that, when AQ is added to an alkaline pulping process or sulphate pulping process, two important phenomena occur, and increase in the rate of delignification and protection of carbohydrate against the peeling reaction by oxidation of the reducing end groups, as a result of which the pulp yield is markedly goes up¹⁹. During pulping, wood degradation is rapid resulting in a loss of about 35% of carbohydrates. The mechanism of this alkaline attack is now well understood and is referred to as the peeling reaction. This process involves the removal of terminal aldonic carbohydrate units until a stopping reaction occurs which stabilizes the polysaccharides against further attack.

Anthraquinone, in catalytic amount, has been postulated as participating in reduction-oxidation reactions. Lowendahl and Samuelson²⁰ explained the effect of AQ addition in soda pulping as being caused by reduction of anthraquinone and reoxidation of the anthrahydroquinone. They concluded that oxidation of reducing sugar end groups in cellulose and hemicellulose to aldonic acid groups is a significant step leading to stabilization of the carbohydrates with respect to endwise alkaline degradation. However, late findings of Vuorinen²¹ suggest that the introduction of aldonic groups is marginal and that corresponds to less than 1% of all the AQ reactions during pulping. Additionally, he suggests that the oxidation reactions by AQ cause little or no increase in the carbohydrate yield during alkaline pulping. It is known that addition of anthraquinone during alkaline cooking leads to oxidation of reducing sugar and groups in the wood during the early stages of the cook²³⁸. This reaction stabilizes the carbohydrate against and wise degradation and leads to the formation of anthrahydroquinone which is then reoxidise to anthraquinone by reacting with lignin at 80-100⁰ C²²⁻²⁷. This stabilization of carbohydrates leads to higher yields as well as increased delignification. Thus AQ act as an organic catalyst in the process. Increased delignification in AQ pulp could be also due to more pronounced cleavage of beta-aryl other linkage in phenolic units²⁸ of wood lignin. Though the hydrosulphide ions also causes cleavage of beta-aryl and other linkage in phenolic units, but it seems that, a small amount of AQ enhances cleavage there by giving more delignified pulp.

MATERIAL AND METHODS: With a view to optimise pulping operations, sulphate chemical pulping (AQ) for *Morus nigra* was studied. The dried debarked logs of *Morus nigra* are converted into chips, the chips were screened and allowed to pass through 22 mm diameter holes and those retained on 5 mm diameter holes were collected for sulphate chemical treatment and 0.05% anthraquinone is added to it, than alkali treatment is done. Cooking temperature kept at 165⁰ C and treatment time was fixed at 2.0, 1.5, 1.0 and 0.5 hrs. In the same way the permagnate number and pulp yields determined in separate analysis.

Determination of permagnate number: The Permagnate number or Kappa number (K. No.) is the number of milliliters of decinormal potassium permagnate solution (0.1N KMnO₄) which is absorbed by 1.0 gm of pulp under certain specified and controlled conditions. This permagnate oxidation is a measure of the lignin content of the pulp and consequently a measure of bleach demand. The permagnate number is therefore useful in determining the extent of delignification of chemical pulps after digestion and in intermediate stages of bleaching. In order to determine the K. No. in the present study 1.0 gm of oven dry pulp was taken in a beaker containing 1200 ml of distilled water and it was stirred to get homogeneous solution. 40 ml of each solution of KMnO₄ (0.1N) and H₂SO₄ (4N), was added to it and was allowed to stir for five minutes. Than potassium iodide solution was added to stop the reaction. The solution so obtained was titrated against hypo (0.1N) solution using starch as indicator and the value of K. No. obtained using the sample relation.

K. No. = 40 – ml hypo consumed.

Determination of pulp yield: 100 gm of chips on dry basis were taken in a perforated yield box and it was placed in the middle of digester while loading the digester. On completion of cooking, chips were taken out of yield box and after washing, disintegration and screening dried in a ventilated oven at 100±5⁰ C overnight. The dried samples were weighed and yield was determined on original weight of chips taken.

RESULTS AND DISCUSSION: The observed values of active alkali, pulp yield and permagnate number (K. No.) of *Morus nigra* are recorded in Table 1 and represented by various graphs plotted between pulp yields, K. No. and effect of anthraquinone on active alkali.

From the results of various parameters determined and presented in Table 1 and as shown graphically in Figures 1 and 2, the analysis of results of *Morus nigra* reveals that when pulp of *Morus nigra* is treated with 15% of active alkali without the addition of AQ for 2 hrs at the temperature 165^o C, the K. No. is 22.2 and pulp yield is 57.2%. But on adding the 0.05% anthraquinone, the K. No. slightly lowers (18.9) and

with reducing the active alkali percentage from 15 to 11, the pulp yield and K. No. shows an increase (Figures 1 and 2). It is also clear that when the active alkali percentage is taken as 15, the temperature is at 165^o C and anthraquinone is kept constant at 0.05%, the K. No. increases and pulp yield also increase (56.8 to 59.9%), on reducing time from 2.0 to 0.5 hrs.

Table 1: Anthraquinone sulphate chemical pulping of *Morus nigra*.

Cook number	Active alkali (%)	AQ (%)	Temperature (° C)	Time (hrs)	Permagnate number (K.No.)	Total pulp Yield (%)
1	15	0.00	165	2.0	22.2	57.2
2	15	0.05	165	2.0	18.9	56.8
3	14	0.05	165	2.0	19.7	57.7
4	13	0.05	165	2.0	20.6	58.7
5	12	0.05	165	2.0	21.7	59.5
6	11	0.05	165	2.0	23.0	60.3
7	15	0.05	165	1.5	20.1	58.2
8	15	0.05	165	1.0	22.0	59.1
9	15	0.05	165	0.5	22.8	59.9

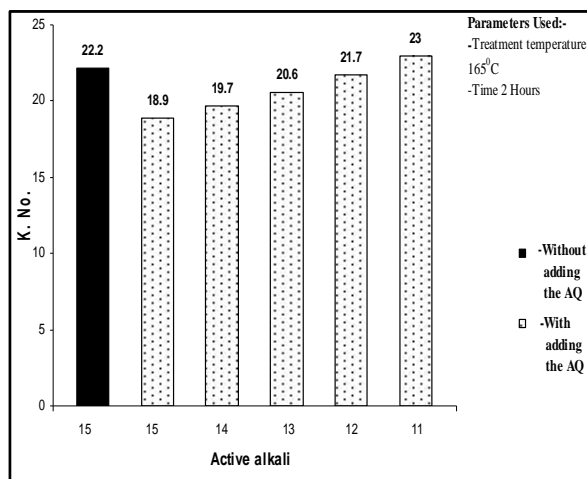


Figure 1: Effect of AQ on active alkali and K. No. of *Morus nigra*.

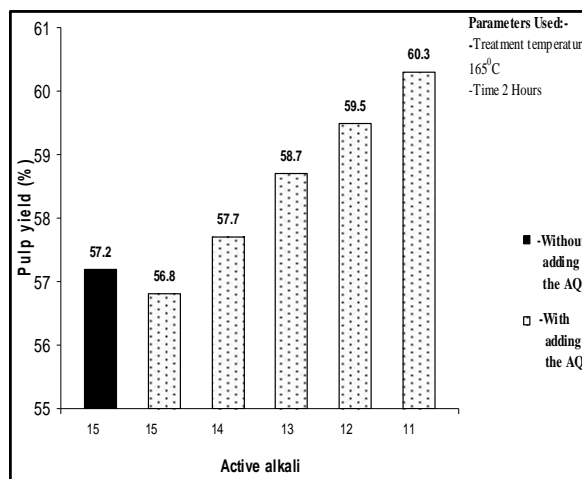


Figure 2: Effect of AQ on active alkali and pulp yield of *Morus nigra*.

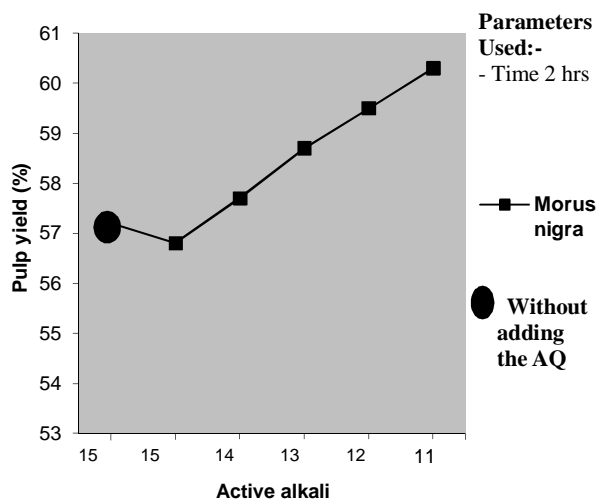


Figure 3: Effect of AQ on active alkali and pulp yield of *Morus nigra*.

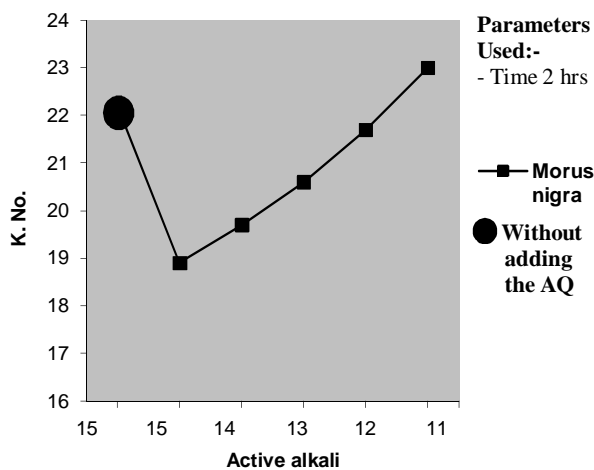


Figure 4: Effect of AQ on active alkali and K. No. of *Morus nigra*.

From Figure 3, it is evident that on reducing the active alkali percentage at treatment temperature 165°C and treatment time 2.0 hrs, the pulp yield is increases. It also reflects from the Figure 4, that on adding the anthraquinone the value of K. No. is rapidly decreases and on reducing the active alkali percentage, the K. No. value again slowly increases in the *Morus nigra* sample. On using active alkali 15%, anthraquinone 0.05%, at the temperature 165°C and on reducing the treatment time the pulp yield increases regularly. But percentage of pulp yield is found higher in *Morus nigra* sample. These results and observations show similarity with the findings of Agarwal and Garg³⁰,

Yamashiki et al.³¹, Tyagi et al.³², Chai et al.³³ and Hedjazi et al.^{34 & 35}.

CONCLUSION: In view of foregoing discussions, it may be concluded that, the lignification of the main fibre wall is less intense in hardwoods like *Morus nigra* and less energy is needed for fibrizing. It is also revealed that results in dissolution of holocellulose, mainly the hemicelluloses increase in alkali consumption. In the anthraquinone sulphate chemical pulping, the dosages of AQ depend upon the type of wood, whether that is a hardwood or softwood. Because of lower lignin content in hardwood like *Morus nigra*, the AQ dosages cannot be more than 0.05%. When pulping is at low K. No., it is necessary to take into consideration not only the economical and environmental reasons, but also to keep in mind that equivalent yields should be attend as well as to avoid the degradation of the fibres in order to preserve or improve the strength properties of the pulp. Addition of AQ can reduce the K. No., this reduction on the residual lignin in the pulp will ensure a better bleachability and uses of less amount of bleaching chemicals. Carbohydrate protection can be obtained by addition of AQ, due to the synergistic effect on the yield increase. It may also be concluded that on addition of a little amount of AQ, the quantity of pulp yield increases and consumption of soda reduces. There is no adverse effect left by anthraquinone (AQ), but it is helpful in reducing the cost of pulp.

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