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New approach for upgrading pulp & paper quality: Mild potassium permanganate treatment of already bleached pulps

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ABSTRACT

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The present work introduces mild – room temperature – potassium permanganate treatment of cellulosic materials, namely already bleached pulps. Such treatment represents a new approach for upgrading pulp and paper quality, which is lacking in the literature. Potassium permanganate was investigated as a purifying and mild oxidizing agent for commercial already bleached softwood and bagasse pulps. It was found that treatment of the bleached beaten pulps, with 0.25–2% KMnO₄ (based on pulp weight), led to significant improvement in paper properties. The strength (breaking length) increased greatly and the brightness increased significantly due to treatment. The improvements were related to the degree of polymerization, and to the alphacellulose content of pulps.

Moreover, potassium permanganate serves as a disinfectant and deodorizer. Thus treatment of bleached pulps with KMnO₄ is a promising remedy for the side effects which pulps suffer, during transportation and storage, before papermaking.

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1. Introduction and object

Potassium permanganate (KMnO₄) is one of the most popular reagents used in analytical chemistry. It is used as an oxidizing agent in diverse chemical reactions in the laboratory and in industry. In the field of pulp and paper, KMnO₄ is used for estimation of the so-called "permanganate number". This number is a measure of pulp bleachability. It equals the amount of permanganate consumed by one gram of moisture-free pulp under specified conditions. Permanganate number is correlated to lignin content of the unbleached pulp. Although other bleaching agents such as hypochlorite and peroxide are used for pulp bleaching, potassium permanganate has only drawn a little attention in this direction (Mobarak, 1981; Krause, 1971).

Recent trends of applying total chlorine-free (TCF) pulp bleaching have dominated; to satisfy the new rules of environment authorities. Therefore, it became appropriate to intensify work on permanganate bleaching, as a chlorine-free bleaching method (e.g. Mobarak, 1981; Krause, 1971; Zhou et al., 2004; Shubakov et al., 2002; Lystd & Soteland, 1996).

In previous work, we have used permanganate as a bleaching agent for bagasse pulp. The results showed that permanganate bleaching is superior to conventional one step hypochlorite bleaching. In addition, the paper strength properties improved due to permanganate bleaching (Mobarak, 1981).

As a mild oxidizing agent, permanganate could be used not only for bleaching, but also for upgrading the properties of already bleached pulps, and hence upgrading the quality of paper made therefrom. This is achieved via manipulating the purifying, and mild oxidizing effects of permanganate. Such studies are lacking in the literature.

The present work aims at investigating the effect of mild KMnO₄ treatment on properties of already bleached pulps, namely bleached softwood and bagasse pulps. Our target is to make use of the mild oxidizing capacity of KMnO₄ for upgrading these bleached pulps and upgrading the quality of paper made therefrom.

Moreover, potassium permanganate also serves as a disinfectant and deodorizer. Therefore, it is thought that treatment of bleached pulps with $KMnO_4$, at mild suitable conditions, might help getting rid of the side effects which the pulps suffer during transportation and storage before papermaking.

2. Materials and methods

Bleached softwood pulp was the first raw material selected for this study. It was kindly provided by Rakta Pulp and Paper Company, Alexandria, Egypt. This pulp was provided in sheet form.

The second raw material selected for this work was a bleached bagasse pulp. It was also provided by Rakta Company in wet form.

We have carried out the chemical and physical analyses for these commercial already bleached pulps. The results of these analyses are reported in Table 1.

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Table 1Analysis and physical properties of the commercial already bleached softwood and bagasse pulps

Pulp type	Bleached softwood	Bleached bagasse
Ash content %	0.48	0.8
Alphacellulose %	85.50	68.10
Alkali extractable hemicellulose %	8.27	25.01
Degree of polymerization (DP)	621	495
Water retention value (WRV) AD %	74.60	131.40

2.1. Treatment with potassium permanganate (Mobarak, 1981)

The proposed treatment is conducted after beating the pulp to 30° SR. The beaten non-dried pulp is then treated with KMnO₄ under the same conditions used for the determination of permanganate number. Treatment with KMnO₄ was conducted as follows: the pulps were stirred in dilute sulfuric acid solution (0.2 N) for 5 min, at room temperature. Potassium permanganate 0.25–2% (based on pulp weight) was then added drop-wise from a burette while stirring, along a period of 5–15 min; depending on the amount of the added permanganate. After addition of permanganate, 5–15 ml of 3% H₂O₂ is added to get rid of the brownish color of manganese oxide hydrate. The pulps were then filtered, and the filtrate was titrated against 0.1 N thiosulfate for estimating the excess permanganate. The pulps were then washed with distilled water and forwarded to papermaking.

2.2. Paper sheet making

The paper sheets were prepared according to the SCA standard, using the SCA – model sheet former (AB Lorenzen and Wetter).

2.3. Determination of centrifugal water retention value (WRV)

Water retention values were determined according to the modified German Standard Method (Jayme, Ghoneim, & Krueger, 1958; Merkblatt IV/33/57/).

3. Results and discussion

3.1. Experiments on bleached softwood pulp

(Table 2) shows the properties of paper sheets made from bleached softwood pulp treated with different amounts of potassium permanganate.

Treatment of the bleached softwood pulp with $KMnO_4$ oxidizes and removes some of the non-cellulosic materials present in the pulp. It also oxidizes the remaining hemicellulose and lignin in situ. This explains the great improvement in breaking length, the decrease in water retention value (WRV), and the improvement of brightness.

It is worth mentioning that treatment with KMnO₄ increases the alphacellulose percentage in the pulp to some extent. However,

Table 2Properties of paper made from bleached softwood pulp treated with different amounts of potassium permanganate

Amount of KMnO ₄ g/100 g pulp	Breaking length in meters	% increase in breaking length	Brightness %	WRV %
None(untreated)	3606	_	71.13	74.60
0.25	3749	3.97	72.88	73.50
0.50	3775	4.69	75.75	62.90
1.00	3809	5.63	75.18	53.30
1.50	4047	12.23	72.90	59.20
2.00	4526	25.51	72.63	63.30

raising the amount KMnO4 to (1.5 g/100 g of pulp) or higher led to a decrease in the alphacellulose. (Table 3) shows the alphacellulose content of the softwood pulp before and after treatment with different amounts of KMnO₄.

It is clear from Table 3 that treatment of the softwood pulp by increasing amounts of KMnO₄ up to (1 g/100 g of pulp) resulted in some increase in alphacellulose of the treated pulp. This increase in the alphacellulose indicates that some of the non-cellulosic materials – present in the pulp – were oxidized, dissolved and washed out during the treatment; leading to an increase in the percentage of alphacellulose. Thus KMnO₄ treatment exerted a purifying effect on the bleached pulp. However, treatment of the wood pulp with 2% KMnO₄, based on pulp, decreased the degree of polymerization (DP) considerably and hence decreased the alphacellulose content of the treated pulp.

(Table 4) illustrates that treatment of softwood pulp with $KMnO_4$ led to a decrease in the DP from 621 (for untreated pulp) to 421 for pulp treated with 2% $KMnO_4$. In other words, the DP of softwood pulp decreased by more than 32% due to treatment.

However, the oxidized hemicellulose and lower DP Cellulose – produced due to treatment – act as strength promoters. This is reflected by the percentage increase in breaking length of the prepared paper sheets, which reached 25% at treatment with 2% KMnO₄ (see Table 2).

It can be safely concluded that the great increase in breaking length of paper due to KMnO₄ treatment of the already bleached soft wood pulp, coupled with the better brightness of the treated pulp, recommend a one step KMnO₄ treatment of already bleached beaten pulps, as a successful means for upgrading the bleached pulps. In addition, potassium permanganate serves as a disinfectant and deodorizer. Thus the treatment of bleached pulps with KMnO₄ is a promising remedy for the side effects which pulps suffer, during transportation and storage, before papermaking.

3.2. Experiments on bleached bagasse pulp

In these experiments, the bleached bagasse pulp was treated with different amounts of KMnO₄, after beating the pulp to 30°SR, under the same conditions used for determination of permanganate number, and as mentioned in the experimental part.

(Table 5) shows the properties of paper sheets made from bleached bagasse pulp treated with different amounts of potassium permanganate. It is clear from Table 5 that the strength properties of paper was improved due to treatment of the pulp with

Table 3Effect of treatment with potassium permanganate on alphacellulose content of the commercial already bleached softwood pulp

Amount of KMnO ₄ g/100 g pulp	Alphacellulose %	$\%$ increase in alphacellulose due to treatment with KMnO $_4$
None (untreated)	85.50	-
0.25	88.50	3.51
1.00	88.00	2.92
1.50	85.80	0.35
2.00	82.60	- (% decrease 3.39)

Effect of treatment with potassium permanganate on the DP of the commercial already bleached softwood pulp

Amount of KMnO ₄ g/100 g pulp	DP	% decrease in DP due to treatment with KMnO ₄
None (untreated)	621	-
1.00	495	20.29
2.00	421	32.21

Table 5Properties of paper made from bleached bagasse pulp treated with different amounts of potassium permanganate

Amount of KMnO ₄ g/100 g pulp	Breaking length in meters	% increase in breaking length	Brightness %	WRV %
None (untreated)	3610	_	68.73	131.40
0.25	5000	38.50	72.00	130.50
0.50	5670	57.06	74.97	122.20
1.00	6403	77.37	72.17	127.10
1.50	6702	85.65	72.00	129.70
2.00	7386	104.60	72.07	130.70

Table 6Effect of treatment with potassium permanganate on alphacellulose content of the commercial already bleached bagasse pulp

Amount of KMnO ₄ g/100 g pulp	Alphacellulose %	% increase in alphacellulose due to treatment with KMnO ₄
None (untreated)	68.10	-
1.00	69.40	1.91
2.00	70.10	2.93

Table 7Effect of treatment with potassium permanganate on the DP of the commercial already bleached bagasse pulp

Amount of KMnO ₄ g/100 g pulp	DP	% decrease in DP due to treatment with KMnO ₄
None (untreated)	495	-
1.00	430	13.13
2.00	346	30.10

KMnO₄, under the mild conditions, which we specified and selected after several preliminary experiments. The brightness, also, fairly improved.

The tremendous increase in breaking length of paper made from the bagasse pulp due to treatment with $\rm KMnO_4$, coupled with the better brightness of the treated pulp, recommend a one step $\rm KMnO_4$ treatment of already bleached beaten pulps as a successful mean for upgrading the pulps.

It is clear from Table 6 that treatment with $KMnO_4$ increases the alphacellulose percentage in the pulp to some extent. This increase in the alphacellulose indicates that some of the oxidized non-cellulosic materials – present in the pulp – dissolved and were washed out during the treatment, leading to an increase in the percentage of alphacellulose.

(Table 7) illustrates that treatment of bagasse pulp with $KMnO_4$ led to a decrease in the DP from 495 (for untreated pulp) to 346 for pulp treated with 2% $KMnO_4$. In other words, the DP of bagasse pulp decreased by more than 30% due to treatment.

Oxidized hemicellulose and lower DP Cellulose – produced due to treatment – acted as strength promoters. This is reflected by the great percentage increase in breaking length of the prepared paper sheets (see Table 5).

4. Conclusions

This study offers a new approach for upgrading pulp and paper quality through mild treatment – of already bleached pulps – with potassium permanganate, at room temperature. Such study is lacking in the literature. The great increase in strength (breaking length) of paper made from the commercial already bleached softwood and bagasse pulps, coupled with the better brightness of the treated pulps, recommend a one step KMnO₄ treatment of already bleached beaten pulps, as a successful means for upgrading the pulps.

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