# UNDERSTANDING OF HEDP USED AS CHELATOR IN PULP BLEACHING

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This study investigated the use of a water treatment agent, 1-hydroxy ethylidene-1,1-diphosphonic acid (HEDP), as chelator in the $O_PQP$ bleaching sequence of *Acacia mangium* kraft pulp. The results showed that the effect of HEDP in bleaching is better than that of EDTA with respect to pulp viscosity, and HEDP is similar to EDTA and DTPA as regards other properties under the same chelating conditions. The optimum Fenton reaction conditions were as follows: temperature of 60 °C, hold time of 30 min, $Fe^{2+}$ to $H_2O_2$ concentration ratio of 1:30, and $H_2O_2$ concentration of 10 mM. Under these conditions, it was found that the chelating ability of HEDP was between those of EDTA and DTPA. In addition, HEDP has the ability to scavenge hydroxyl radicals, whereas DTPA does not have this ability in the $UV/H_2O_2$ irradiation system.

*Keywords*: 1-hydroxy ethylidene-1,1-diphosphonic acid (HEDP), pulp bleaching, chelator, Fenton reaction, hydroxyl radicals

## INTRODUCTION

Hydrogen peroxide is used as a brightening and delignifying agent in elementary chlorine-free (ECF) and totally chlorine-free (TCF) bleaching sequences. Transition metals, such as Fe, Mn and Cu, catalyze the decomposition of hydrogen peroxide, which leads to the loss of active hydrogen peroxide and a decrease in pulp strength. The formation of non-selective species, *i.e.* hydroxyl radicals, leads to selective chromophore elimination and improved delignification. However, hydroxyl radicals also result in the inevitable degradation of polysaccharide chains. This degradation can remove hydrogen atoms from cellulose, which leads to a loss of pulp viscosity.

Traditionally, inorganic salts of magnesium and silicate are used to stabilize alkaline hydrogen peroxide in an effort to reduce the effects of hydroxyl radical formation during the bleaching process. Closure of the water loops is limiting the use of silicates as stabilizers in the bleaching of mechanical pulp. Some studies concerning the use of zeolites as peroxide stabilizers have been conducted. Zeolites alone do not function as very good stabilizing agents;[1-3] however, the brightness gains are similar to those obtained with DTPA. In a study by M. Sain *et al.*,[4] zeolite-supported chemicals indicated improved chelation and peroxide stabilization compared to an optimum dosage of a conventional DTPA/Na-silicate system. In addition, commonly used chelators include sodium salts of EDTA and DTPA, with alternative chelators being developed.[5,6] The main concerns regarding chelators are the low biodegradability and difficulty of removal from bleach plant effluents. Studies on ethylenediamine disuccinic acid (EDDS) and iminodisuccinic acid (IDS) as biodegradable chelators in pulp bleaching have already been conducted.[7,8] IDS serves as a decent biodegradable alternative for EDTA or DTPA, especially in the bleaching of high-yield pulps.[9] However, the stability constants of IDS for iron and manganese are somewhat lower than those of EDTA or DTPA.[10]

In this work, 1-hydroxy ethylidene-1,1-diphosphonic acid (HEDP) as a chelator was used in the Q stage during the $O_PQP$ bleaching sequence. The role of HEDP used as chelator in pulp bleaching will also be discussed. HEDP itself can be biodegradable in compared with EDTA in acidic environments. The ozonation of HEDP in basic conditions results in the formation of phosphorus-containing intermediate by-products, which can remove the transition metals effectively from pulp.[11] In addition, HEDP also has the advantage of corrosion inhibition, anti-scaling performance, and low cost. These particular advantages demonstrate the importance of this research.

## EXPERIMENTAL
### Materials and chemicals

*Acacia mangium* kraft pulp was obtained from APRIL SSYMB, located in Shandong province, China. The pulp, as received, had a kappa number of 27.17 and an intrinsic viscosity of 1016 mL/g. The pulp was screened (slit-width of 0.25 μm) thoroughly and then washed with distilled water.

EDTA2Na (disodium ethylene diamine tetraacetate), DTPA (diethylene triamine pentacetate acid) of analytical grade were purchased from Sinopharm Chemicals Reagent Co. Ltd., China. HEDP (1-hydroxy ethylidene-1,1-diphosphonic acid) of analytical grade was purchased from Shandong Taihe Water Treatment Co. Ltd., China. $H_2O_2$ (hydrogen peroxide), salicylic acid of analytical grade were purchased from Northpharm Chemical Co. Ltd., China.

### $O_P$QP bleaching sequence conditions

Hydrogen peroxide-reinforced oxygen delignification was performed using a CRS 1030 bleaching reactor (Wenrui Machinery, Shandong, China). The pulp was bleached at 100 °C for 1 h under an oxygen pressure of 0.5 MPa. Other bleaching conditions were as follows: NaOH, $H_2O_2$ and $MgSO_4$ charges of 3.0%, 1% and 0.3% of O.D. pulp, respectively.

The chelation stage ($Q_1$-$Q_3$) was performed in sealed plastic bags at 60 °C in a thermostatic water bath. The pulp was diluted to 10% consistency using distilled water. The initial pH value was kept at 3 and the final pH value was approximately 4 for the Q stage with EDTA, DTPA and HEDP individually. After 30 min, the pulp was thoroughly washed with distilled water and then dewatered.

The hydrogen peroxide bleaching stage was conducted in a thermostatic water bath at 90 °C. The pulp at a 10% consistency was sealed in a plastic bag with 4% $H_2O_2$, 2% NaOH, 2% $Na_2SiO_3$ and 0.3% $MgSO_4$ (based on O.D. weight). The bag was then immersed under water for 180 min.

### Fenton reaction

The reaction of iron(II) with hydrogen peroxide ($H_2O_2$) in aqueous solution leads to the formation of hydroxyl free radicals, a powerful, non-selective oxidant. Hydroxyl radicals can react with salicylic acid to produce 2,3-dihydroxy-benzoic acid, which has an absorbance maximum at 529 nm.[12] Through the addition of chelator into the Fenton reaction, the concentration of ferrous iron decreases, which results in the reduction of the hydroxyl radical concentration, and the absorbance of colored substances will decrease.

In this Fenton system, 1 mL of 1.2 mmol/L $Fe^{2+}$, 1 mL of 40 mmol/L salicylic acid solution and 1 mL deionized water were added to different test tubes. The absorbance of the above aqueous solutions was measured at 529 nm against a reference sample after reaction with 1 mL of 40 mmol/L $H_2O_2$ for 30 min. This paper discusses the process conditions of the Fenton reaction with chelator addition (HEDP, EDTA, or DTPA) into this reaction system.

### UV/$H_2O_2$ reaction system

Sample solutions were prepared using 100 mM $H_2O_2$ and 2.5 mM acetovanillone. The solution pH was adjusted by adding dilute acid/alkali at 60 °C for 30 min, and then the UV-visible absorption spectra of acetovanillone were determined using a UV-2550 system (Shimadzu, Japan). The oxidizing ability of the UV/$H_2O_2$ system may be attributed to the formation of OH·. The absorbance as a function of irradiation time was recorded after the addition of chelators (HEDP, DTPA or EDTA) to UV/$H_2O_2$.

### Pulp and paper properties

The kappa number, viscosity, and brightness of all pulp samples were determined according to TAPPI standards. The HexA (hexenuronic acid) content of the pulp samples was determined according to the HUT method. Handsheets were made from pulp following the procedure of TAPPI Test Methods T205 sp-12 and the tear index, tensile index, and burst index were determined according to TAPPI Test Methods T220 sp-10.

## RESULTS AND DISCUSSION
### Pulp properties

As shown in Table 1 and Table 2, the application of a 3.0% NaOH charge on OD pulp at 90 °C resulted in reductions of kappa number and viscosity values of 67.84% and 37.60%, respectively. The brightness increased from 28.76% to 57.78% ISO. The HexA content of the kraft pulp and the $O_P$ pulp was of 11.86 and 4.72 mmol/kg, respectively. In accordance with previous studies, the influence of HexA on the kappa number was calculated based on the assumption that 10 mmol/kg pulp of HexA is equivalent to one kappa number unit.[12-16] The corrected kappa numbers for the kraft pulp and the $O_P$ pulp were 25.98 and 8.28, respectively.

The $O_P$ pulp treated with HEDP was better with that treated with EDTA or DTPA. The kappa number of the pulp subjected to the $O_PQP$ bleaching sequence was not corrected because the content of HexA was small and therefore can be neglected. Comparing with EDTA and DTPA, HEDP was found to be capable of producing an improvement in the strengths of the handsheets, especially in burst and tear indexes, following the treatment with the $O_PQP$ sequence.

**Fenton reaction system**

The efficiency of the Fenton reaction is illustrated in Figure 1 to Figure 4, as depending on the $H_2O_2$ concentration, $[Fe^{2+}]/[H_2O_2]$ ratio, pH, and reaction time. The optimal conditions for the Fenton reaction were defined at a $[Fe^{2+}]/[H_2O_2]$ ratio of 1:30, because when the ratio $[Fe^{2+}]/[H_2O_2]$ is equal to 1/20, the absorbance is 0.871, which is beyond the measurement accuracy range of the UV absorption spectrum.

Table 1
Properties of pulp during various bleaching sequences

| Sequences | Kappa number | Viscosity (mL/g) | Brightness (% ISO) | P.C. number (%) | HexA content (mmol/kg) |
|---|---|---|---|---|---|
| KP pulp | 27.17±0.31 | 1016±7 | 28.76±0.07 | — | 11.86±0.01 |
| $O_P$ stage | 8.75±0.13 | 825±5 | 57.78±0.03 | — | 4.72±0.00 |
| $O_PQ_{HEDP}P$ | 5.85±0.19 | 716±4 | 82.03±0.01 | 1.176±0.01 | 2.04±0.02 |
| $O_PQ_{DTPA}P$ | 6.06±0.10 | 686±6 | 80.26±0.01 | 1.087±0.02 | 1.56±0.01 |
| $O_PQ_{EDTA}P$ | 6.18±0.17 | 697±4 | 80.14±0.00 | 0.999±0.02 | 1.86±0.01 |

Note: Post color (P.C.) number is used for analysis of brightness reversion by comparing brightness before and after reversion, simply counting the brightness points lost, according to the formula:
P.C. number $= ((k/s)_{after\ ageing} - (k/s)_{before\ ageing}) \times 100$
The values for k (light absorption coefficient) and s (light scattering coefficient) are calculated by the formula:
$k/s = (1 - R_\infty)^2/2R_\infty$ (Kubelka-Munk)

Table 2
Properties of paper during various QP stages

| Bleaching with different chelators | Basis weight (g/m²) | Folding resistance | Burst index (kPa·m²/g) | Tear index (mN·m²/g) | Tensile index (N·m/g) |
|---|---|---|---|---|---|
| $O_PQ_{HEDP}P$ | 62.6±0.7 | <5 | 1.30±0.01 | 3.96±0.13 | 26.7±0.1 |
| $O_PQ_{DTPA}P$ | 62.8±1.1 | <5 | 1.26±0.06 | 3.64±0.16 | 26.3±0.1 |
| $O_PQ_{EDTA}P$ | 61.5±0.8 | <5 | 1.24±0.05 | 3.62±0.12 | 25.9±0.0 |

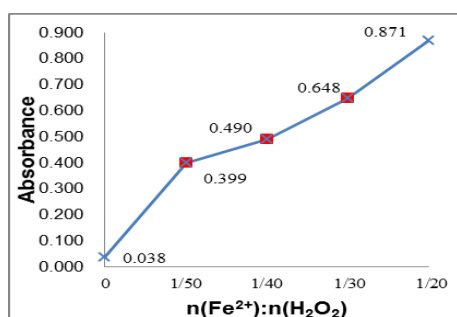Note: none of the bleached pulp samples was beaten



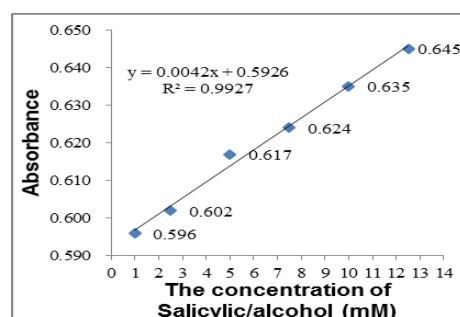Figure 1: Effect of $n(Fe^{2+})$:$n(H_2O_2)$ on absorbance



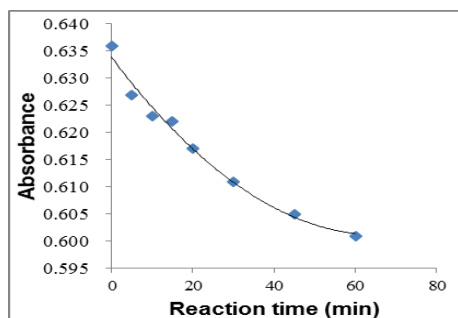Figure 2: Effect of salicylic acid/alcohol concentration on absorbance

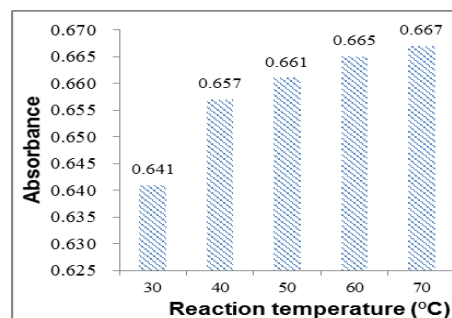Figure 3: Effect of reaction time on absorbance


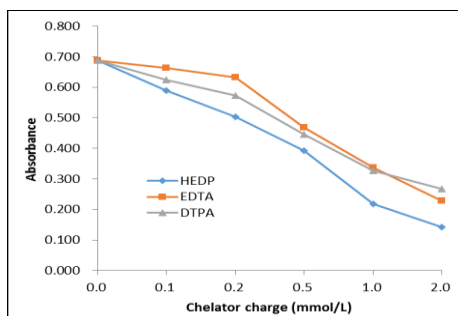Figure 4: Effect of system temperature on absorbance
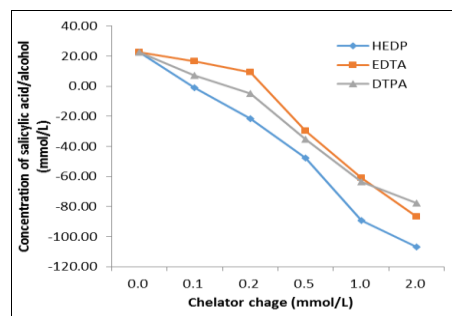

Figure 5: Effect of chelator charge on absorbance


Figure 6: Effect of chelator charge on concentration of salicylic acid/alcohol

Increasing the reaction time from 0 to 60 min decreased the absorbance; a temperature increase from 30 to 70 °C did not considerably affect the absorbance. Considering the temperature and time of the chelating stage ($O_PQP$ bleaching sequence), the optimal reaction time and temperature were of 30 min and 60 °C, respectively. The absorption at 529 nm was read after 30 min at 60 °C.

Figure 2 shows that the absorbance can be expressed as a function of salicylic acid/alcohol concentration (mM) using Eq. 1, based on the curve in the graph:

$y = 0.0042x + 0.5926$ (1)

where y is the absorbance and x is the salicylic acid/alcohol concentration.

**Effect of chelators on Fenton reaction**

As shown in Figures 5 and 6, all chelator agents reduced the absorption of the solution, and this effect increased with increasing concentration. Moreover, at a concentration greater than 0.1 mmol/L, the absorbance slopes with HEDP are considerably steeper than those with DTPA and EDTA, as indicated in Figure 5. The analysis of the metal ions content could help explain some of the results listed in Table 1. Because HEDP is a chelator, it chelated upon addition to the Q stage and removed a large percentage of the metal ions during washing, thereby helping to produce a higher brightness and viscosity at a given dosage.

**UV/$H_2O_2$ oxidation system**

Dilute solutions of acetovanillone (2.5 mM) were fairly soluble in 100 mM $H_2O_2$. A pKa value of 7.81[17] was determined with the UV-2500 spectrophotometer by recording changes in the absorbance as a function of the solution pH value. As can be seen in Figure 7, in the absorbance curves for acetovanillone, the pH value of the solution exceeds 10.89, but the absorbance at 342 nm is relatively constant. As long as the pH of the reaction system was greater than 10.89, the absorbance at 342 nm could be used to measure the concentration of acetovanillone. Figure 8 illustrates the absorbance of acetovanillone at different molar concentration; the fitted curve was y = 25.115x + 0.0013, and $R^2$ = 0.9928 showed the equation could adequately describe the relationship between the adsorption and concentration of acetovanillone.
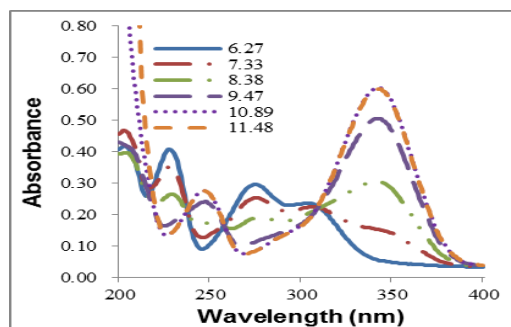
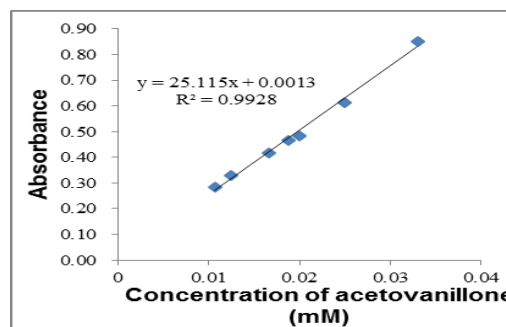Figure 7: Effect of pH value on UV-visible absorbance spectra of acetovanillone



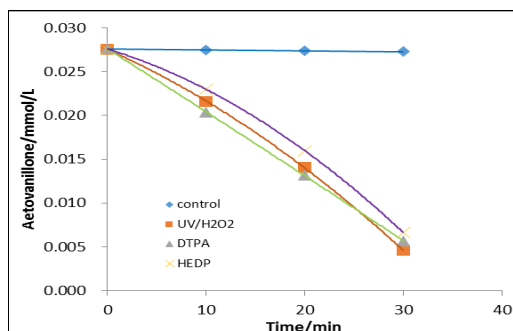Figure 8: Absorbance of acetovanillone solution at 342 nm and pH 11.12



Figure 9: Effect of time on concentration of acetovanillone with various chelators (ultraviolet lamp operated at 2.5 A, 250 V, lamp to sample distance of 21 cm and dosage of DTPA and HEDP of 2.0 mmol/L

Compared to the hydrogen peroxide reaction with acetovanillone without UV irradiation, the slopes of the control reaction for the concentration of acetovanillone remained essentially flat; these results can also be seen graphically in Figure 9. In other words, the degradation of hydrogen peroxide does not occur in the acetovanillone solution without catalyst ($Fe^{2+}$, $Cu^{2+}$, $Mn^{2+}$) or UV irradiation. The formation of OH radicals is directly facilitated by the photolysis of $H_2O_2$,[18] and increasing the reaction time of UV/$H_2O_2$ further reduces the acetovanillone concentration, as indicated by the red line in Figure 9. Surprisingly, it was observed that the addition of HEDP to UV/$H_2O_2$ had an impact on the acetovanillone concentration. In addition, the slope for UV/$H_2O_2$ with HEDP lies between that for the control and that for UV/$H_2O_2$. That is to say, HEDP can scavenge a certain amount of hydroxyl radicals; however, DTPA does not have this ability.

**CONCLUSION**

1. The results from the $O_P$ pulp chelated with HEDP are similar to the results from the pulp chelated with DTPA or EDTA. HEDP has the advantage of low cost over DTPA and EDTA.

2. The Fenton reaction experiment indirectly confirmed that the chelating ability of HEDP can be ranked between those of DTPA and EDTA, which can explain that the pulp properties are similar between $O_PQ_{HEDP}P$ and $O_PQ_{DTPA}P$ or $O_PQ_{EDTA}P$ bleaching sequence.

3. HEDP can be used as hydroxyl radical scavenger in a UV/$H_2O_2$ system, while DTPA does not have the same effect.

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