

BLEACHING OF COTTON WITH PERACETIC ACID IN THE PRESENCE OF METAL IONS

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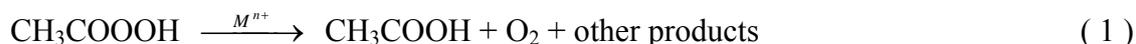
ABSTRACT

Bleaching of cotton fibers with peracetic acid (PAA) could be an economic and environmentally safe alternative for bleaching. Optimal conditions for the process are 60 °C and an initial pH of 7.5, set with sodium carbonate. At these conditions, PAA has the highest activity although only little PAA is consumed in the process. The goal of our research was to increase the consumption and to exploit PAA to a higher extent. Research was focused on the effect of metal salts and its complexes containing copper, zinc and iron. The influence of catalysts was assayed by measuring the rate of PAA consumption and/or decomposition. Catalytic activity of metal salts and their complexes was found to be the highest for copper and the lowest for iron ions (Cu>Zn>Fe). Copper ions have a higher activation effect giving greater PAA consumption and a better bleaching effect.

1. INTRODUCTION

Peracetic acid (PAA) is well established as an oxidant in the food and paper industries and in textile industry for the laundering of linen. The main advantage of bleaching with PAA instead of hydrogen peroxide is that a satisfactory degree of whiteness can be achieved in 40 minutes at 60°C and neutral pH without the addition of auxiliary agents (Križman et al. 2005). Its use in the textile industry is limited due to its poor stability in solution and its sharp smell.

PAA is produced industrially by mixing acetic acid and hydrogen peroxide in the presence of an acid catalyst. Since the reaction is in equilibrium, commercial products contain a certain amount of acetic acid and hydrogen peroxide. PAA spontaneously decomposes in water at higher temperatures and higher pH to give acetic acid and oxygen as main products, but the decomposition can also be caused by heavy metal ions (e.g. M^{n+}), especially when single-electron transfers are possible (Reaction 1):

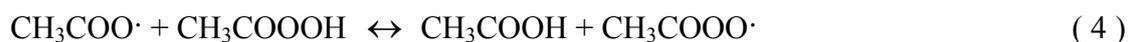


The reaction leads to the formation of products that may have no bleaching action (Yuan and Heinningen, 1997).

The bleaching action of PAA occurs as it is shown in Reaction 2:



Hydrogen peroxide in the presence of metal ions is converted to a hydroxyl radical ($\text{HO}\cdot$) and a hydroxide ion (OH^-). If this metal ion is iron, the reaction is called the Fenton reaction. Excessive amounts of radicals are harmful to cellulose because of their high reactivity. Radical damage can be significant because it can proceed as a chain reaction. The peroxy radical formed from PAA is highly reactive as well and can react in a chain reaction (Reactions 3-7).



We have to consider that transition metal ions may react with both PAA and hydrogen peroxide to form oxygen-based radicals that are very reactive and have the ability to form, among other compounds, epoxides that can be converted to diols (Hashem et al. 2003).

In addition oxygen formed in these reactions (Reactions 1 and 6) could be in the singlet state and as such responsible for bleaching too.

Some transition metal ions are capable of activating hydrogen peroxide and peroxy acids and thus accelerating the bleaching process. Because of their high catalytic activity, we may add only a small amount of transition metal ions.

Suitable metal ions are found to be manganese, titanium, iron, cobalt, nickel and copper, with special preference being given to manganese (Wieprecht et al., 2005; Hashem et al., 2003).

Using metal complexes instead of metal salts does not cause any appreciable damage to fibers and does not interfere with subsequent dyeing. Metal complexes are used for improving action of peracetic acid in the bleaching of stains on textile material, in washing solutions with antibacterial activity, in the pre-treatment with textile bleaching agents, as catalysts in selective oxidation reactions, in wastewater treatment, in delignification of cellulose and bleaching of the pulp etc. (Wieprecht et al., 2005).

Since phthalocyanines are industrial dyes, metallophthalocyanines are an attractive alternative as readily available oxidation catalysts. Iron and manganese phthalocyanine catalysts were found to be less active in oxidation reactions than metalloporphyrins (Meunier and Sorokin, 1997).

Metallophthalocyanines can be used to catalyze the oxidation of chelating agents and their complexes with hydrogen peroxide (Pirkanniemi et al. 2003).

The goal of this research was to increase the consumption of PAA and to exploit PAA at bleaching of cotton fibers to a higher extent. At the same time, good whiteness degree with negligible fiber damage by using bleach catalysts should be achieved. Metal salts and complexes of copper, iron and zinc were used as catalysts.

2. EXPERIMENTAL PROCEDURES

2.1 Materials

Scoured and desized cotton fabric, 102 g/m², was obtained from Tekstina, Slovenia. Peracetic acid (PAA) was supplied as a 15% equilibrium solution in the commercial

bleaching agent Persan S15, obtained from Belinka, Slovenia. Sodium carbonate was obtained from Carlo Erba, Italy. Copper, iron and zinc phthalocyanines were obtained from Sigma Aldrich (Germany), while their salts (copper sulfate, iron(III)nitrate and zinc acetate) were obtained from Kemika Zagreb (Croatia) or Merck-Alkaloid Skopje (Macedonia).

2.2 Bleaching

Bleaching of scoured cotton fabric was performed in flasks in a shaking water bath (SWB25, Haake) at a frequency of 85 rpm and constant temperature of 60°C. The bleaching bath contained 15 ml/l of Persan S15 in distilled water. The liquor ratio was 1:20 and the initial pH value of 7 was adjusted by the addition of solution of Na₂CO₃. After that 0,75 ppm of copper, iron and zinc ions were added. After 120 minutes of bleaching, the fabric was washed in hot water and rinsed twice in cold water. The samples were air-dried.

2.3 Methods

2.3.1 Concentration of reactants

The rate of PAA and hydrogen peroxide decomposition and consumption in the bleaching bath was monitored by iodometric titration. A method developed in the Laboratory for Peroxide Chemistry in the Faculty of Chemistry and Chemical Technology, University of Ljubljana, was used to determine the concentration of both oxidants.

This method is based on the reaction of both PAA and hydrogen peroxide with potassium iodide. The released iodine was titrated with standardized sodium thiosulphate. Since both oxidants react with potassium iodide at room temperature, the titration provided total oxidant concentration. To determine the PAA concentration, titration with sodium thiosulphate was performed on ice (0°C) since hydrogen peroxide reacts very slowly with potassium iodide at this temperature. The calculated difference between total oxidant and PAA concentration was equal to hydrogen peroxide concentration.

All values reported were the average of at least two readings.

2.3.2 Whiteness

The degree of whiteness was measured on a remission spectrophotometer (Datacolor Spectraflash SF600 Plus) using the CIE method, according to EN ISO 105-J02:1997 (E).

2.3.3 Damage to substrate

Fibers damage was determined by measuring the degree of polymerization (DP-values) with the viscosimetric method. For this purpose, fibers were dissolved in cuoxam.

3. RESULTS AND DISCUSSION

Decomposition and consumption of PAA and hydrogen peroxide

The concentration of PAA and hydrogen peroxide was monitored in 15 minutes intervals over 120 minutes at constant temperature (60°C) and pH (pH 7).

Persan S15 was added to the bleaching bath first, followed by sodium carbonate solution to adjust the initial pH, while metal ions were added at the end.

The pH was monitored during bleaching and remained unchanged in almost all cases. Only in the case of iron ions, the pH decreased to 6,5.

It was expected that in the presence of metal ions the rate of decomposition of both PAA and hydrogen peroxide would increase. In Figures 1a and 1b, it is shown that the catalysts used do not have the ability to increase the decomposition and consumption with regard to the blank sample. Only in the case of copper salts the decomposition of PAA increased considerably (Figure 1a).

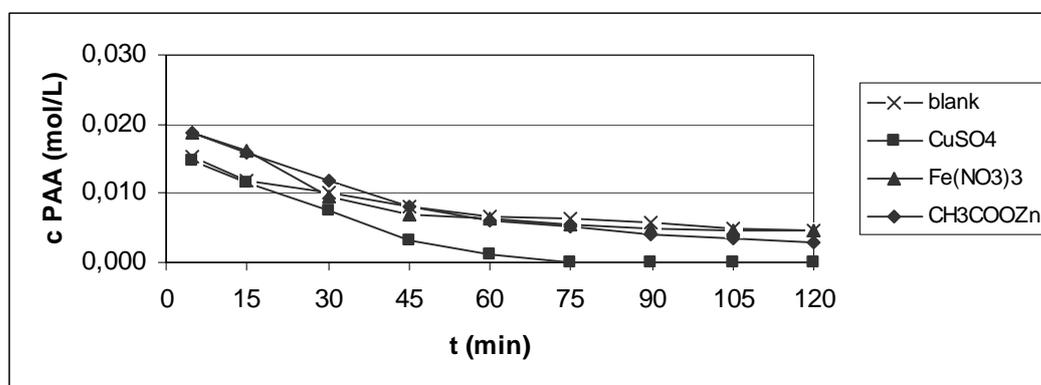


Figure 1a: Change in concentration of PAA with time in the bleaching bath at pH 7, at temperature of 60°C and with different metal salts

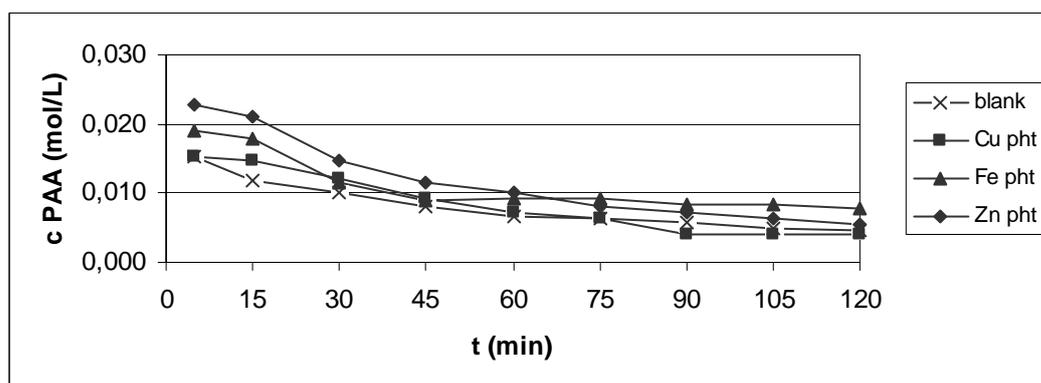


Figure 1b: Change in concentration of PAA with time in the bleaching bath at pH 7, at temperature of 60°C and with different metal complexes

Several researchers claim that when compared to cobalt and manganese, iron is the third most powerful catalyst, being stronger than copper and other metal ions (Yuan et al. 1997; Koubek et al., 1963). However, we have to consider that they studied the consumption of PAA in the presence of iron salts other than iron (III) nitrate. We noticed that iron (III) nitrate has only little effect on decomposition of PAA (Figure 1a).

We can conclude that the decomposition depends mainly on the type of the salts used and on the valence state of the iron ion.

In Figures 1a and 1b it is also shown that the initial PAA concentration (after 5 min of the addition of PAA) is higher when catalysts are present. It seems that at the onset of bleaching the catalysts have a stabilizing effect on PAA.

The initial concentration of hydrogen peroxide remains the same in almost all cases; exceptions are cases with copper salts where the consumption is higher (Figure 2a), and zinc phthalocyanine where the decomposition of hydrogen peroxide is lower (Figure 2b).

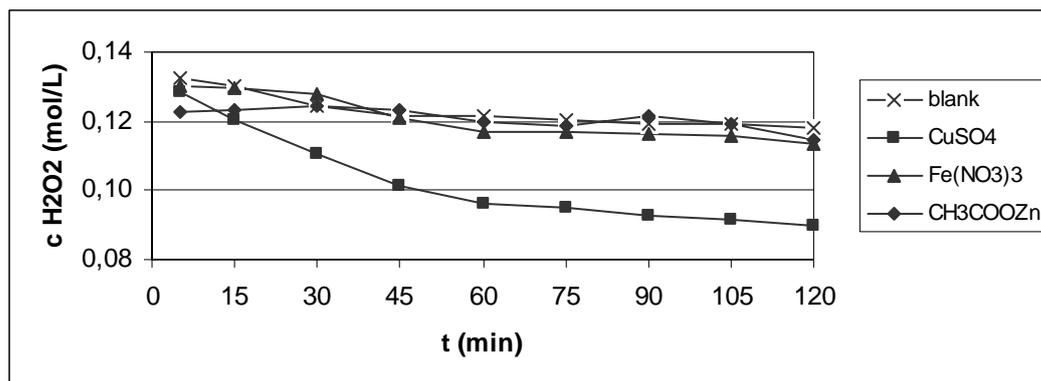


Figure 2a: Change in concentration of H₂O₂ with time in the bleaching bath at pH 7, at temperature of 60°C and with different metal salts

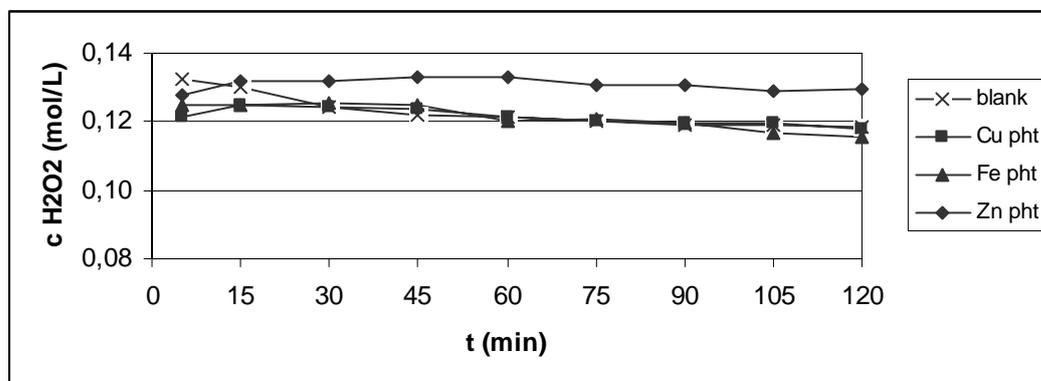


Figure 2b: Change in concentration of H₂O₂ with time in the bleaching bath at pH 7, at temperature of 60°C and with different metal complexes

Comparing all figures, we can conclude that the metal ion complexes have lower catalytic activity than metal salts.

Whiteness and damage of cotton substrate

Whiteness and degree of polymerization of bleached cotton samples are summarized in Table I:

Table I. Whiteness, average degree of polymerization (DP) and Eisenhut's tendering factor (TF) for samples bleached at 60°C over 120 minutes at pH7 in the presence of

different catalysts.

| Catalyst added | Whiteness | Damage | TF |
|-----------------------------------|-----------|--------|------|
| Unbleached | 15,9 | 2845 | - |
| Blank* | 76,8 | 2350 | 0,20 |
| Fe(NO ₃) ₃ | 64,8 | 2324 | 0,21 |
| CH ₃ COOZn | 81,0 | 2370 | 0,19 |
| CuSO ₄ | 82,4 | 936 | 1,28 |
| Fe (II) phthalocyanine | 76,7 | 2304 | 0,22 |
| Zn phthalocyanine | 78,8 | 2419 | 0,17 |
| Cu phthalocyanine | 80,2 | 2291 | 0,23 |

*A blank sample is a scoured fabric bleached without the addition of a catalyst.

The whiteness degree achieved using copper and zinc catalysts was higher than the whiteness degree of the blank sample. Metal salts gave a higher whiteness than corresponding metallophthalocyanines. This confirms that the catalytic activity of complexes is lower than the catalytic activity of salts. A relatively low whiteness was achieved in the case of iron catalyst, mainly due to yellowness caused by adsorption of hydrolyzed iron salts. With iron phthalocyanine the achieved whiteness was higher, but still lower when compared to the blank sample.

Comparing all three types of metallophthalocyanine the same conclusion can be made: copper phthalocyanine as catalysts gave the highest degree of whiteness, followed by zinc and iron phthalocyanine.

Figure 5 shows that during the first 10 minutes whiteness increased rapidly, after that the increase is almost negligible. When copper salts were present, the same whiteness was achieved in 40 minutes as in the blank bath in 120 minutes.

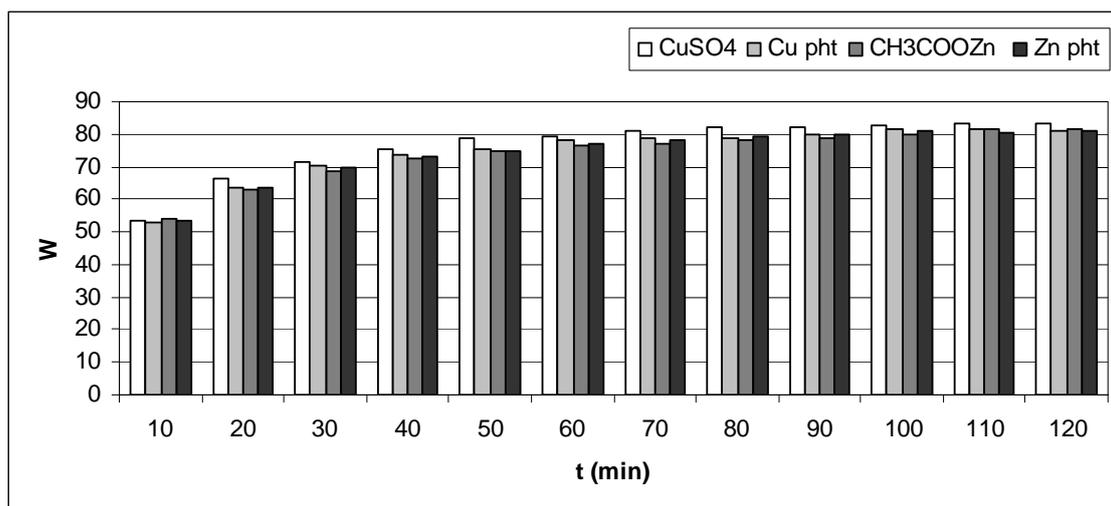


Figure 5: Change in degree of whiteness with time for samples bleached at 60°C and initial pH 7 in the presence of different catalysts.

The highest DP values and consequently the lowest damage had the samples bleached in the presence of small amounts of metallophthalocyanines. Lower DP values obtained in the presence of metal salts compared to those obtained in the presence of

metallophthalocyanines show the possibility that metal salts cause the formation of OH[·] radicals, which are responsible for greater decrease of cotton DP. Severe damage of fibers was most prominent when copper ions were present.

Eisenhut's Tendering factors, which were calculated from DP by comparing with unbleached sample (2845), reveal that only copper salts must be avoided.

4. CONCLUSIONS

Peracetic acid is an efficient oxidant for bleaching cotton. It gives a satisfactory degree of whiteness at 60°C and neutral pH without the addition of auxiliary agents. However, a high residual content of both PAA and hydrogen peroxide remains in the bleaching bath unused, which leads to a waste of chemicals and as such must be minimized.

When small amounts of copper ions are present, a higher PAA consumption can be obtained. On the other hand, there is severe fiber damage. We can conclude that copper ions as catalysts for bleaching with PAA should be excluded.

The use of iron ions must be avoided too, because of the yellowness that they cause.

An alternative is the use of zinc ions as catalysts. We obtained an excellent whiteness with no severe fiber damage. However, when using zinc ions, a high content of both PAA and hydrogen peroxide still remains in the bleaching bath unused.

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