A Novel Method for the Determination of Hydrogen Peroxide in Bleaching Effluents by Spectroscopy

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A spectrophotometric method for the determination of hydrogen peroxide in pulp bleaching effluents is reported. The method is based on hydrogen peroxide instantly reacting with vanadium pentoxide in sulfuric acid solution, forming a peroxovanadate complex that has an absorption maximum at 454 nm. It was found that the optimum conditions were as follows: detection wavelength of 454 nm, a V_2O_5:H_2O_2 mole ratio of 2.2, and a sulfuric acid concentration of 0.5 mol/L. In order to eliminate the interference from dissolved lignin, fines, and suspended solids, the samples were acidified and centrifuged for spectroscopic quantification. The results showed that the method has an excellent measurement precision (RSD < 0.3%) and accuracy for the quantification of hydrogen peroxide content in pulp bleaching effluents. The present method is simple and accurate, making it suitable for applications in the pulp and paper industry.

Key words: Hydrogen peroxide; Bleaching effluent; Spectrophotometry; Vanadium pentoxide

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INTRODUCTION

Hydrogen peroxide is a strong oxidizer. Due to its oxidizing properties, hydrogen peroxide is used widely as an oxidant, a disinfectant, and a bleaching agent in various industrial and household products (Li *et al*. 1996). In the pulp and paper industry, hydrogen peroxide is mainly used as a bleaching agent for virgin and secondary recycled pulps. It is regarded as "clean" due to its minimal environmental impact (Chai *et al*. 2004). The residual hydrogen peroxide content in pulp bleaching effluents is an important parameter; it plays an important role both in quality control and from an economic perspective during hydrogen peroxide bleaching processes. Therefore, it is necessary to develop a rapid analytical method for the measurement of residual hydrogen peroxide in pulp bleaching effluents.

Traditional methods such as titration (Greenspan and MacKellar 1948; Gordon *et al*. 1992) and spectrophotometry (Chai *et al*. 2004; Graf and Penniston 1980; Dukes and Hyder 1964; Odo *et al*. 2004), as well as advanced techniques, such as chromatographic techniques (Stefan 1998), the chemiluminescence method (Arnous *et al*. 2002), fluorescence determination (Hanson *et al*. 2001; Chen *et al*. 1999), electro-chemical analysis (Yamamoto *et al*. 2000; Wael *et al*. 2012), and the enzymatic method (Gustavsson and Damlin 1999), have been employed for hydrogen peroxide quantification. Titration is the dominant and practical technique used for the determination of hydrogen peroxide in bleaching effluents. However, this method is time consuming and not sufficiently sensitive for samples containing low levels of residual

hydrogen peroxide (Hu *et al*. 2012). Moreover, advanced techniques are expensive, which restricts their applicability in routine testing in a mill setting.

In this study, a simple and rapid spectroscopic method was developed to quantify the hydrogen peroxide content in bleaching effluents. The main focuses were to explore the color reaction conditions (*i.e*., the dosage of color regent and sulfuric acid concentration) and to minimize the spectral interference from the dissolved lignin, fines, and suspended solids in the bleaching effluents. The present method does not require the use of hazardous organic compounds acting as a color reagent in the experiment. It is simple, rapid, and accurate, making it suitable for applications in the pulp and paper industry.

MATERIALS AND METHODS

Chemicals and Samples

All chemicals used in the experiment were obtained from commercial sources. Deionized water was used in solution preparation. A color agent, vanadium pentoxide solution, was prepared by dissolving 0.2 g of V_2O_5 in 100 mL 0.5 mol/L H_2SO_4. The effluent samples were collected from the hydrogen peroxide bleaching process conducted in the laboratory.

Apparatus

All measurements were performed using a UV-Vis spectrophotometer (HP-8453, Hewlett-Packard, now Agilent Technologies, CA, USA) equipped with a 10 mm silica cell.

Analytical Procedures

A 5 mL of each effluent sample was mixed with 1 mL of 0.5 mol/L H_2SO_4 in a vial. After that, the mixture was centrifuged at 8000 rpm for 5 min. A micro-syringe was used to take a measured volume of supernatant and to add it to a 5 mL aliquot of color agent. Mixing of the solution was achieved by manual shaking. The absorption of the resulting solution was measured at 454 nm.

RESULTS AND DISCUSSION

Conditions for Spectrum Analysis

Hydrogen peroxide reacts with vanadium pentoxide in sulfuric acid solution, generating a peroxovanadate complex. The peroxovanadate complex has a red-brown color and absorbs in the UV-Vis range with a maximum absorptivity at 454 nm. Figure 1 shows the UV–Vis absorption spectral of the peroxovanadate complex in the wavelength range of 350 to 750 nm.

As shown in Fig. 1, the absorbance at 454 nm increases with the addition of the amount of hydrogen peroxide. Therefore, hydrogen peroxide can be determined by UV-Vis spectrophotometry through its reaction with an overdose of vanadium pentoxide in sulfuric acid solution.

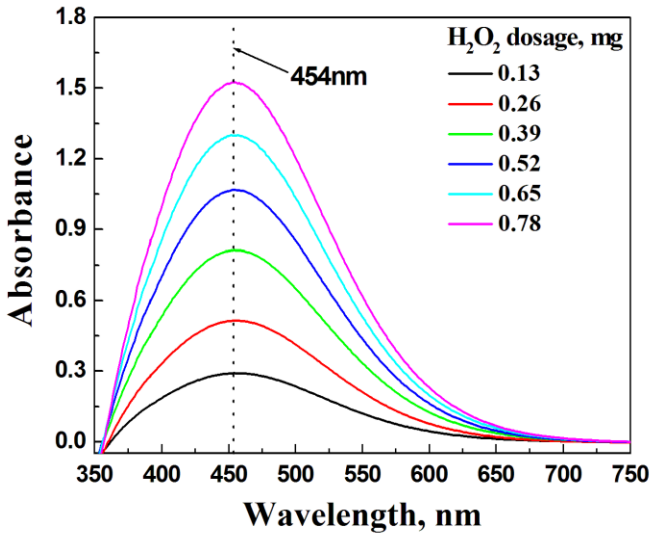

Fig. 1. Absorption spectrum of peroxovanadate complex

Effect of Vanadium Pentoxide Dosage

An excess amount of vanadium pentoxide is necessary for the complete reaction of hydrogen peroxide. The results illustrated in Fig. 2 show that a molar ratio of 2.2-mole vanadium pentoxide to hydrogen peroxide is required to achieve a complete reaction.

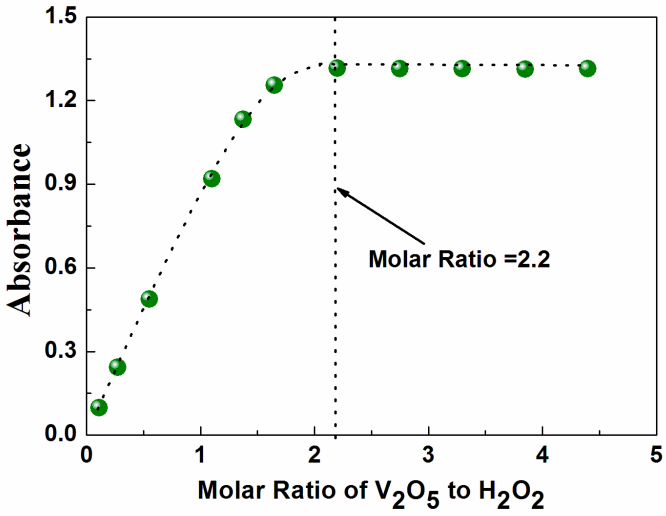

Fig. 2. Effect of vanadium pentoxide dosage

Effect of H_2SO_4 Concentration

Figure 3 shows the effect of sulfuric acid concentration on the color reaction. It can be seen that to insure a complete reaction at the given conditions, the concentration of sulfuric acid added should not be less than 0.5 mol/L. Therefore, 0.5 mol/L of sulfuric acid was used in subsequent studies.

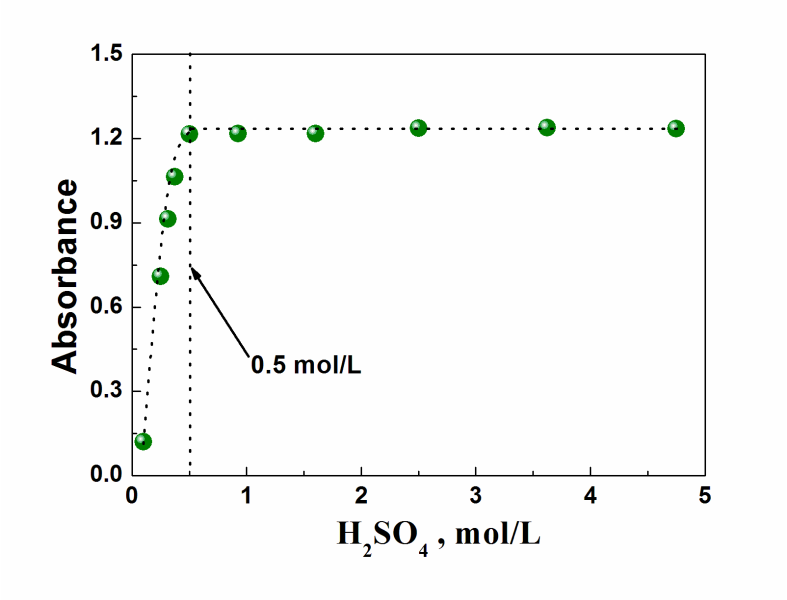

Fig. 3. Effect of H_2SO_4 concentration

Determination of Hydrogen Peroxide

A simple standard calibration can be developed for hydrogen peroxide determination in aqueous solutions based on the measurement of the absorbance of the peroxovanadate complex in the solution. In this work, the calibration curve was obtained based on adding different contents (0 to 0.9 mg/L) of standard hydrogen peroxide solution in color reagent. According to the data from measuring these samples, a standard calibration curve was obtained. The results are shown in Fig. 4.

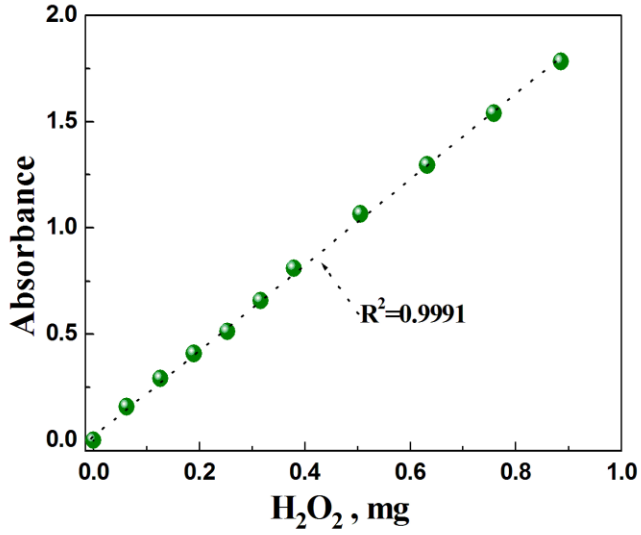

Fig. 4. Standard calibration curve

Based on Beer's law, the content of hydrogen peroxide in the sample can be calculated according to the following equation,

$$C = \frac{k}{V} A_{454} \quad (1)$$

where C represents the content of hydrogen peroxide (in mg/L) and V represents the sample volume (in mL) added to the 5 mL of color reagent. The factor k is 0.488 mg, which is obtained from the calibration graph shown in Fig. 4. The parameter A_{454} represents the absorbance at 454 nm.

Spectral Interferences

For the determination of hydrogen peroxide in bleaching effluent, the major sources of spectral interference are cations from transition metals such as iron, manganese, and copper. However, to minimize the effect of transition metals on peroxide bleaching activity, iron and other transition metal ions can be removed from pulps by chelating treatment before the hydrogen peroxide bleaching process. Therefore, the effect of these inorganic ions on hydrogen peroxide determination using the spectral characteristics of the peroxovanadate complex can be neglected.

In bleaching effluent, there are many organic species such as dissolved lignin, fines, and suspended solids. They will interfere in the determination of hydrogen peroxide by UV-Vis spectrophotometry. In order to eliminate the interference, the samples were acidified with sulfuric acid and centrifuged. As shown in Fig. 5, the samples had a certain degree of absorption at 454 nm without treatment, whereas the treated sample has almost no absorption. Therefore, it can be concluded that acidification and centrifugation are capable of eliminating interferences from organic species in a typical sample.

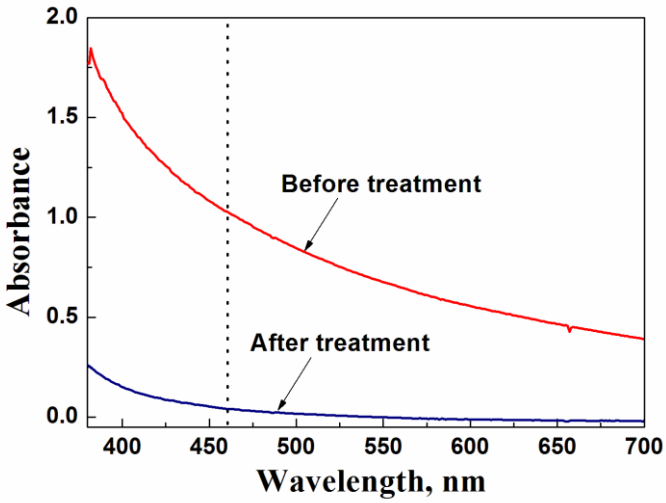

Fig. 5. Absorption spectrum of sample liquor before and after treatment

Method Precision and Validation

The repeatability of the present method was investigated. The results show that the relative standard deviations (RSD) in five measurements were less than 0.3%.

To verify the present method, a set of sample solutions was prepared by accurately spiking different amounts (0 to 4 mg) of hydrogen peroxide into 5.0 mL of

bleaching effluent sample. The original bleaching effluent (*i.e.*, without added hydrogen peroxide) served as the control. The net contribution from the added hydrogen peroxide in the spectrophotometry measurement for these spiked samples can be calculated by Eq. (1). As shown in Table 1, the recoveries achieved in the present method were in the range of 98.3% to 102.0%, which is appropriate for many purposes.

Table 1. Method Validation *****

Sample no.	Amount of H_2O_2, mg		Recovery, %
	Measured	Added	
1	0.746	0.736	101.4
2	1.465	1.472	99.5
3	2.249	2.207	101.9
4	3.003	2.943	102.0
5	3.616	3.679	98.3

***** The amount of H_2O_2 in 5 mL of the original bleaching effluent was 3.5 mg.

CONCLUSIONS

A spectrophotometric method was developed for the determination of hydrogen peroxide in pulp bleaching effluents. The selected conditions were as follows: detection wavelength of 454 nm, a V_2O_5:H_2O_2 mole ratio of 2.2, and a sulfuric acid concentration of 0.5 mol/L. The present method is simple, rapid, and accurate. Therefore, it should be well-suited for use in industrial, as well as laboratory settings.

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