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# Polyoxometalate catalyzed ozonation of chemical pulps in organic solvent media

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ABSTRACT

Polyoxometalate (POM) catalyzed ozonation of chemical pulps in organic solvent media was found to be particularly effective and selective environmentally benign bleaching approach providing a way for substantial increase in pulp brightness, viscosity and degree of delignification in comparison with other ozone-based bleaching techniques. A series of tested low-boiling polar aprotic and protic organic solvents showed a well-defined capacity for ozonation improvement in the presence of Keggin-type heteropolyanion $[PMo_7V_5O_{40}]^{8-}$ (HPA-5). Even moderate solvent proportion of 6% (w/w) in the reaction solution caused additional gain in brightness up to 3.4% ISO with simultaneous increase in pulp viscosity up to 8.8% and lignin removal up to 18.9% after HPA-5 catalyzed ozonation (0.8% $O_3$; 0.5 mM HPA), as compared with the control solvent-free process. An aqueous acetone solution was found to be the preferred reaction medium in terms of pulp brightening and delignification. Under optimized conditions, the POM-catalyzed ozonation of eucalypt kraft pulp in acetone/water solution showed remarkable brightness improvement by 15.1% ISO with additional lignin removal by 39.4% and increase in intrinsic viscosity by 3% in comparison with pulp bleached in water media.



## 1. Introduction

Early transition metal oxygen anion clusters (polyoxometalates or POMs) find a wide application as versatile green catalysts for liquid-phase oxidation of different organic substances [1,2]. Heteropolyoxometalates (free heteropolyacids and salts of heteropolyanions) possessing the properties both of strong acids and of very efficient oxidants hold a great interest now for application as bi-functional catalysts in homogeneous and heterogeneous systems [3–5]. Remarkable features of heteropolyanions (HPAs) such as a high solubility in water and oxygen containing organic solvents, a high stability over a wide temperature and pH range and an ability of easy regeneration (re-oxidation) by molecular dioxygen, hydrogen peroxide and ozone have opened up new possibilities for HPAs utilization as efficient catalysts for environmentally benign (chlorine-free) selective delignification of lignocellulosics [6–8]. Continuous reuse (recirculation) of catalytic solution in a close-loop mode opens the possibility for development of totally effluent-free POM bleaching technology with carbon dioxide and water as the only byproducts after lignin oxidation [6]. The α-Keggin-type mixed-addenda HPAs, such as molybdovanadophosphate heteropolyanions of the series $[PMo_{(12-n)}V_nO_{40}]^{(3+n)-}$, were recognized as the more suitable POMs for oxygen bleaching of chemical pulps [9]. The heteropolyanion $[PMo_7V_5O_{40}]^{8-}$ or HPA-5 showed the best results in terms of delignification. However, the high acidity of the reaction media (pH 1–2) required for optimal catalytic action of HPA-5 affects negatively the carbohydrate complex of bleached pulp, causing undesirable hydrolytic (solvolytic) polysaccharide degradation and respective loss in pulp viscosity [10,11].

The low pH of reaction media limits the HPA-5 application for oxygen delignification, but makes it very attractive for ozone bleaching operating under the same acidic pH range. In HPA-catalyzed bleaching, the extremely high oxidation potential of ozone can substantially reduce the redox cycle of catalyst regeneration in comparison with oxygen or peroxide delignification, thereby providing an accelerated rate of bleaching reactions and a higher efficiency of the bleaching process as a whole.

Ozone is the most powerful and particularly potential oxidation agent in pulp bleaching technology [12]. The ozone bleaching stage, as an integrated part of the advanced totally chlorine-free (TCF) bleaching sequences, was recently applied to different types of conventional (sulfur-based) and unconventional (organosolv) pulps from a wide variety of woods and non-wood (agro-fibre) sources [13–15]. Despite the extremely high reactivity of ozone (oxidizing potential of +2.07 eV [16]), a low selectivity of ozone treatment towards lignin (due to unwanted reactions with cellulose leading to a deterioration of pulp quality) restricts the delignification capacity of ozone and limits its application in pulp bleaching technology as a whole. A variety of different chemicals, so-called "cellulose protectors", has been tested as the additives for reaction solution with an aim to improve ozonation performance. The positive effect of some organic solvents on pulp ozonation has been reported [17–20].

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The selectivity improving of ozone bleaching still remains to be solved in spite of intensive efforts mounted in this field in the last two decades. The change in redox properties of oxidation bleaching system by application of POM catalysis can be a feasible way to increase selectivity and efficiency of pulp ozonation.

Early experiments on HPA-5 catalyzed ozone bleaching in aqueous medium showed promising results in terms of delignification [9], but the substantial loss in pulp viscosity was also revealed, indicating low suppression of radical-induced polysaccharide degradation.

The development of a novel particularly effective and selective pulp bleaching approach using POM-catalyzed ozonation in organic solvents as a reaction media is reported in the present paper. The effect of organic solvent and process variables on ozonation results and POM catalysis is discussed.

## 2. Materials and methods

### 2.1. Materials

Industrial unbleached eucalypt (*E. globulus* L.) kraft pulp (Portucel Mill) with 41.60 ± 0.05% ISO brightness, 2.39 ± 0.03% residual lignin (as Klason and acid-soluble) and an intrinsic viscosity of 1320 ± 2 mL $g^{-1}$ was used. Before bleaching, the pulp was thoroughly washed with deionized water to remove all residual black liquor.

Molybdovanadophosphate heteropolyanion HPA-5 was prepared by stoichiometric reaction of $MoO_3$, $V_2O_5$, $NaH_2PO_4$ and $Na_2CO_3$ according to a previously described procedure [21].

Organic solvents as well as all other chemicals used were of analytical grade purity and purchased by Sigma–Aldrich, Riedel-de Haen and Fluka companies.

### 2.2. Ozonation of kraft pulp

Pulp ozonation (3% consistency; 0.8% ozone charge; pH 2; 20 °C) was performed in a 1 L Fischer glass batch reactor equipped with a high-speed teflon-covered stirrer and connected with a laboratory Fischer-502 ozone generator. After ozonation, pulps were thoroughly washed with deionized water. Acidic pulp treatment with diluted sulfuric acid (pH 2; 30 min) was performed before ozonation to increase ozone selectivity towards lignin. Ozone concentration was measured using a conventional iodometric procedure. Two replicated ozonation were performed for each experimental condition set.

### 2.3. Pulp analysis

Residual lignin content was determined as Klason and acid-soluble lignin according to T 222 om-88 and UM 250 TAPPI standards. Pulp viscosity was measured in cupri-ethylenediamine (CED) solution according to SCAN-CM 15:88 standard. Handsheet formation for physical and reflectance test was performed according to TAPPI T 205 om-88 and TAPPI T 272 om-92 standards, respectively. Physical properties of pulp hand-sheets were examined according to TAPPI T 220 om-88 standard. Pulp optical properties (ISO brightness and DIN 6167 C/2 yellowness index) were measured by CM-3630 Spectrophotometer (Minolta).

The content of aldehyde (CHO) groups in pulps was measured spectroscopically at 546 nm (Shimadzu, UV-160A) after color reaction with 2,3,5-triphenyltetrazolium chloride [22].

Hexenuronic acid (HexA) groups in pulps were quantified by selective hydrolysis in formic acid–sodium formate buffer followed by UV-spectroscopy (Shimadzu, UV-160A) of the formed 2-furoic acid at 245 nm [23].

All measurements were replicated to obtain reproducible data.

Having in mind the economical and technological feasibility of possible chemicals recovery, a few low-boiling polar aprotic (acetone and dioxan) and protic (methanol, ethanol, *n*-propanol and isopropanol) organic solvents were chosen as a potential reaction media for POM-catalyzed ozone bleaching of chemical pulps.

## 3. Results

For solvent screening experiments, the industrial eucalypt (*E. globulus*) kraft pulp was ozonated under fixed conditions of ozone charge and catalyst (HPA-5) concentration in the presence of 6% (by weight) of organic solvent. The brightness development as well as the extent of lignin and carbohydrate degradation during ozonation was examined and compared with control (solvent-free) test.

### 3.1. Comparative effect of different organic solvents on POM-catalyzed ozonation

As can be seen from Table 1, the conventional ozonation in water media (control test) is fairly effective in delignification and brightness development of eucalypt kraft pulp. But, the substantial drop in pulp viscosity (by 30.3%) with respective loss in pulp strength properties (expressed as tear, burst and tensile strength) is also observed, indicating intensive carbohydrate degradation.

The presence of POM (HPA-5) catalyst in aqueous solution has a positive effect on the selectivity of pulp ozonation (see control vs. POM/water, Table 1), by somewhat decreasing residual lignin and increasing pulp viscosity. But the pulp brightness, as the most important bleaching property, is only slightly affected.

It is evident from Table 1, that the addition of organic solvent into the reaction mixture substantially improves POM-catalyzed ozonation. Even a moderate solvent proportion of 6% (w/w) in aqueous solution caused a gain in brightness with simultaneous increase in pulp viscosity and lignin removal in comparison with POM/water and, particularly, with control (water, catalyst-free) ozonation.

Obviously, the bleaching effect depends on the nature of the organic solvent used. The comparative response of pulp to ozone treatment in different reaction media is shown in Figs. 1–3. Four tested solvent-based reaction systems (i.e., methanol-, ethanol-,

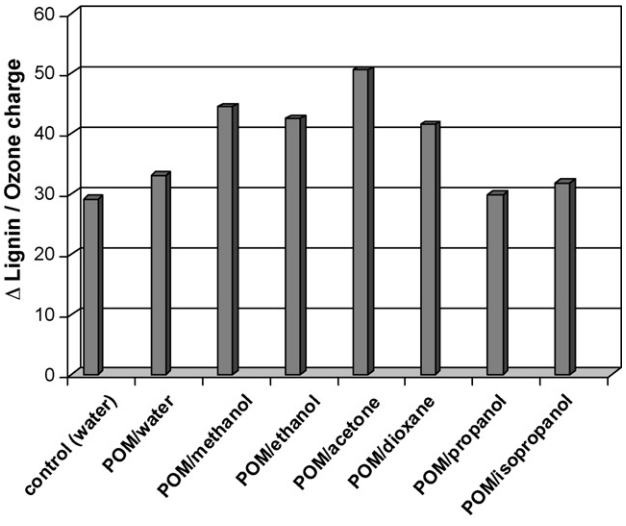


**Fig. 1.** Delignification efficiency of POM-catalyzed pulp ozonation in various reaction media (expressed as lignin decrease per unit of ozone applied). Ozonation conditions: 3% pulp consistency; [$O_3$] = 0.8% odp; [HPA-5] = 0.5 mM; 6% (w/w) solvent concentration; pH = 2.