

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### **Aqueous Oxidation of 2,6-Dimethylphenol with Hydrogen Peroxide Catalyzed by Transition Metal Complexes Supported on Polyvinylpyridinium Salts**

Hany El-Hamshary<sup>ab</sup>; Fahad N. Assubaie<sup>a</sup>

<sup>a</sup> Department of Chemistry, Faculty of Science, King Faisal University, Al-Ahsa, Saudi Arabia <sup>b</sup> Department of Chemistry, Faculty of Science, Tanta University, Tanta, Egypt

Online publication date: 28 January 2004

**To cite this Article** El-Hamshary, Hany and Assubaie, Fahad N.(2004) 'Aqueous Oxidation of 2,6-Dimethylphenol with Hydrogen Peroxide Catalyzed by Transition Metal Complexes Supported on Polyvinylpyridinium Salts', *Journal of Macromolecular Science, Part A*, 41: 2, 107 – 114

**To link to this Article:** DOI: 10.1081/MA-120027297

**URL:** <http://dx.doi.org/10.1081/MA-120027297>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Aqueous Oxidation of 2,6-Dimethylphenol with Hydrogen Peroxide Catalyzed by Transition Metal Complexes Supported on Polyvinylpyridinium Salts

Hany El-Hamshary\* and Fahad N. Assubaie

Department of Chemistry, Faculty of Science, King Faisal University,  
Al-Ahsa, Saudi Arabia

### ABSTRACT

The oxidation of 2,6-dimethylphenol (2,6-DMP) was studied using H<sub>2</sub>O<sub>2</sub> as oxidant catalyzed by some transition metal-salphen complexes, supported on polyvinylpyridinium salts in aqueous solutions. The major product was the diphenoquinone (DPQ). No reaction products were obtained when the reaction was carried out in the absence of polymers. The effects of reaction parameters such as the type of the polymeric support, concentration of H<sub>2</sub>O<sub>2</sub>, pH, and metal-catalyst were investigated in terms of percent conversion and product distribution of the starting materials. The methyl-poly-4-vinyl-pyridinium iodide (PVP-MeI) supported Mn-salphen was the most reactive catalyst system while the *n*-butyl-poly-4-vinyl-pyridinium bromide (PVP-BuBr) supported Cu-salphen was the most selective catalyst.

*Key Words:* Polymeric support; Polyvinylpyridinium salts; Salphen complexes; Phenols; Oxidation.

\*Correspondence: Hany El-Hamshary, Department of Chemistry, Faculty of Science, Tanta University, Tanta 31527, Egypt, E-mail: hany\_elhamshary@hotmail.com.



## INTRODUCTION

Phenolic compounds constitute an important class of organic contaminants commonly found in the subsurface. These compounds are the primary wastewater treatment challenge found in the aqueous effluents from petroleum refineries, coal conversion processes, petrochemical production, and the production of phenols and related chemicals, are listed among the 25 most frequently detected groundwater contaminants at hazardous waste sites.<sup>[1]</sup> Methods of phenol removal include sorption over natural surfaces like activated carbon,<sup>[2]</sup> or sorption over organophilic clay that was modified with organic polymers.<sup>[3]</sup> However, removing some organic pollutants by sorption only is not always enough and the need to oxidize or reduce them to less harmful products is necessary. Oxidative coupling of phenols could prove to be a novel in-situ approach to soil and groundwater remediation that would result in reduced treatment times and costs.<sup>[4]</sup> Oxidative coupling of phenols using chemical reagents like hydrogen peroxide, permanganate molecular oxygen, and ozone, are widely used.<sup>[5,6]</sup> Hydrogen peroxide has the advantage of producing oxygen and degrades biologically.<sup>[7,8]</sup>

Transition metal complexes chemically bound to an insoluble polymeric support have become one of the most popular methods to overcome problems of homogeneous catalysis.<sup>[9-11]</sup> Resins based on polymers of 2- and 4-vinylpyridines have been used successfully as supports for various reagents and catalysts for the oxidation and/or destruction of phenols.<sup>[12-14]</sup>

In the present study we are supporting different metal complexes of *N,N'*-bis-*o*-salicylaldiminesulfonic acid disodium salt (M-salphen) supported on different alkyl poly-4-vinylpyridinium (PVP) salts and investigating their catalytic behavior for the aqueous oxidation of 2,4- and 2,6-dimethylphenols (2,4-DMP and 2,6-DMP) as model water pollutants.

## EXPERIMENTAL

### Materials

Phenols, 2,6-DMP, 2,4-DMP, and *N,N'*-methylenebisacrylamide (Merck) were used as received. 4-Vinylpyridine (Aldrich) was distilled under reduced pressure before use. The water soluble metal complexes of *N,N'*-bis-*o*-salicylaldiminesulfonic acid disodium salt (M/salphen) was prepared as described elsewhere.<sup>[15]</sup> The chloride and sulfate salts of Mn<sup>II</sup>, Fe<sup>II</sup>, and Cu<sup>II</sup> used for ligand metallation were of reagent grade and used as received.

### Preparation of Crosslinked Copolymers

Crosslinked PVP was prepared by solution polymerization in toluene of 8 mol% 4-vinylpyridine and 2 mol% *N,N'*-methylenebisacrylamide as crosslinking agent, using 1 wt% benzoyl peroxide as initiator. The solid polymer was filtered off, washed with methanol and diethylether and dried under vacuum for 24 h. FTIR spectra



(KBr) showed absorptions at  $1590\text{ cm}^{-1}$  (CH=N pyridine unit), and at  $2920\text{ cm}^{-1}$  (CH<sub>2</sub> chain).

### Quaternization of Poly-4-vinylpyridine

In a typical run, PVP (50.0 mmol) was swelled in 50.0 mL of absolute methanol and 75.0 mmol of methyl iodide was then added. The reaction mixture was refluxed at  $80^{\circ}\text{C}$  for 48 h. The produced polymeric salt was filtered off and washed with methanol. The product was characterized by elemental analysis of the halide content using the Volhard method<sup>[16]</sup> and IR spectral data.

Crosslinked copolymer of acrylamide and 4-vinylpyridine (PAM-PVP) was prepared by free radical solution polymerization, according to a standard procedure.<sup>[17]</sup> Acrylamide 4.644 g (65 mmol) and *N,N'*-methylenebisacrylamide 0.308 g (2 mmol) dissolved in 5 mL of methanol, and 4-vinylpyridine 3.423 g (33 mmol) in 85 mL of toluene were placed in 250 mL flask. The polymerization started by the addition of 5 mL of 1.0 wt% benzoylperoxide solution in toluene and the reaction mixture was heated at  $80^{\circ}\text{C}$  for 12 h. The solid polymer was filtered off, washed with methanol, and diethylether and dried at  $50^{\circ}\text{C}$  under vacuum for 24 h. The prepared polymers were characterized by elemental analysis of the nitrogen content (% N found 12.0), and FTIR spectra (KBr) which showed absorptions at  $3340\text{ cm}^{-1}$  (NH amide),  $1645\text{ cm}^{-1}$  (C=O amide),  $1590\text{ cm}^{-1}$  (CH=N pyridine unit), and at  $2920\text{ cm}^{-1}$  (CH<sub>2</sub> chain).

The produced copolymer was quaternized using methyl iodide in a similar way used to prepare PVP polymeric salts.

### Catalytic Phenol Oxidation

Oxidation experiments of the dimethylphenols were conducted in a 100-mL glass reactor and stirred with a magnetic stirrer. In a typical experiment the polymeric catalyst was prepared by the addition of aqueous M-salphen solution drop wise with stirring to about 38.0 mL of water containing the polymeric support. The polymer amount was adjusted to give polymer to catalyst ratio of 10. The pH was adjusted with 5.0 mL buffer. It was then added a solution of phenol (3.0 mmol) dissolved in 5.0 mL of methanol. The reaction was started by injecting 3 mmol of H<sub>2</sub>O<sub>2</sub> (30% aqueous solution), where the total reaction volume was 50.0 mL. The total volume of the reaction mixture was maintained at 50.0 mL. The reactions were run for 24 h at  $30^{\circ}\text{C}$  under air, and the course of the reaction was monitored by TLC. At the end of the reaction, the solid polymer was separated by filtration, and washed with methylene chloride. The organic products were extracted from the filtrate by methylene chloride (3 × 25 mL), and combined with the washings and the solvent evaporated under vacuum. The reaction products were identified by elemental microanalysis and IR spectra, and by comparison with authentic samples.

A blank catalytic oxidation experiment was carried out in the absence of polymeric support.

In a separate experiment ultrafiltration of the reaction mixture before starting, the oxidation showed traces of the metallic salphen in the filtrate, which indicate that almost all of the catalyst amount was bound to the polymeric support.



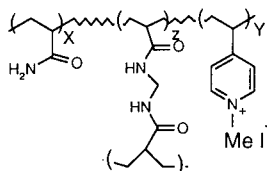
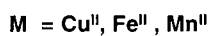
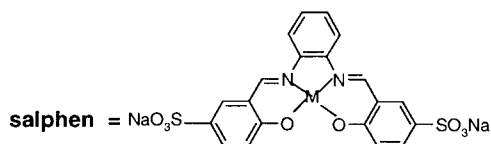
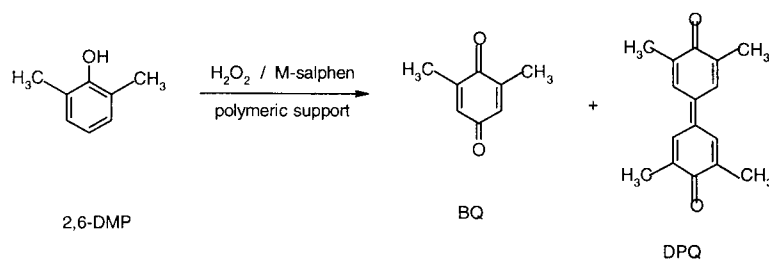
## RESULTS AND DISCUSSION

## Polymeric Supports

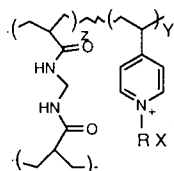
Resins based on polymers of 2- and 4-vinylpyridines have been used successfully as supports for various reagents and catalysts for the oxidation and/or destruction of phenols.<sup>[12-14]</sup> We have prepared PVP and polyacrylamide-co-4-vinylpyridines and quaternized them with alkyl halide having different chain length; methyl iodide, and *n*-butyl bromide (Sch. 1), following standard procedures to give polymeric salts with ~95% conversion. The obtained polymeric salts have hydrophilic polyelectrolyte properties like methyl-poly-4-vinyl-pyridinium iodide (PVP-MeI), *n*-butyl-poly-4-vinyl-pyridinium bromide (PVP-BuBr), and polyacrylamide-co-4-vinyl methylpyridinium iodide (PAM-PVP-MeI).

## Catalytic Oxidation

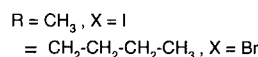
The polymeric pyridinium salts were used as supports in very small amounts ~0.05 g for metal complexes of *N,N'*-bis-*o*-salicylaldiminesulfonic acid disodium salt (M-



**PAM-PVP-MeI**



**PVP-R X**



**Scheme 1.** Oxidation of 2,6-DMP.



salphen) in the aqueous oxidation of 2,6-DMP using hydrogen peroxide as oxidizing agent. The catalyst was bound to the polymeric support as indicated from ultrafiltration of the reaction mixture. The molar ratio of H<sub>2</sub>O<sub>2</sub> to catalyst was 130. The predominant products formed in the oxidation reactions were 2,6-dimethyl-*p*-benzoquinone (BQ) and 3,3'-5,5'-tetramethyl-diphenoquinone (DPQ) (Sch. 1). The efficiency of the polymeric catalysts is presented as the percentage of DMP conversion and percentage of formation of DPQ and BQ.

The oxidation results reported in Table 1 indicate a gradual increase in the percent conversion of 2,6-DMP as the number of carbons in the alkyl groups increase from methyl to *n*-butyl. The maximum conversion of about 58% was observed for PVP-BuBr supported Cu-salphen. This increase in percent conversion going from PVP-MeI to PVP-BuBr may be explained as an increase of the amount of phenol absorbed from the aqueous phase by the more hydrophobic polymer PVP-BuBr. Such an increase of the amount of phenol in the polymer phase allows easier interaction between the phenol and the catalytic sites located in the polymer, hence the conversion of phenol to give increased products. However, such a conversion was greatly reduced on going to the highly hydrophilic hydrogel polymeric salt PAM-PVP-MeI, probably due to a decrease in the amount of the hydrophobic phenol within the polymeric domain. Thus, the opportunity of interacting with the catalytic sites distributed in the polymer was decreased. On the other hand, although such a reduction in the amount of phenol reacted with PAM-PVP-MeI catalyst system; it was greatly affected the product distribution to give the DPQ in addition to the major product BQ observed before with PVP-MeI and PVP-BuBr in almost comparable ratio. No products were obtained when catalytic reactions were carried out in the absence of polymers.

We also tried to oxidize 2,4-DMP. However, the attempt to oxidize 2,4-DMP did not succeed with either PVP-MeI or PVP-BuBr, probably due to blocking of the *para*-position of the hydroxyl group and the resonance at the *ortho*-position to give products.

**Table 1.** Oxidation of 2,6- and 2,4-DMP using Cu-salphen supported on different polymeric salts.<sup>a</sup>

Polymeric support	% Conversion of DMP <sup>b</sup>	% Selectivity <sup>b</sup>	
		BQ	DPQ
No polymer added	0.0	0.0	0.0
PVP-MeI	47.8	97.4	2.6
PVP-BuBr	58.4	98.2	Traces
PAM-PVP-MeI	41.2	55	45
PVP-MeI	0.0 <sup>c</sup>	—	—
PVP-BuBr	0.0 <sup>c</sup>	—	—

<sup>a</sup>All reactions were carried out using  $4.6 \times 10^{-3}$  M of polymeric pyridinium support,  $6 \times 10^{-2}$  M of DMP, ( $4.6 \times 10^{-4}$  M) Cu-salphen, and  $6.0 \times 10^{-2}$  M of H<sub>2</sub>O<sub>2</sub>. Reactions were done in the presence of 5 mL of borate buffer pH 9. The reaction time was 24 h.

<sup>b</sup>Percent conversion based on isolated products.

<sup>c</sup>2,4-Dimethylphenol.



### Effect of Metal

Many metals have special oxygen transfer properties which improve the utility of hydrogen peroxide through generating the highly reactive hydroxyl radicals (OH). The effect of variation of metal on the catalytic activity was tested using Cu<sup>II</sup>, Fe<sup>II</sup>, and Mn<sup>II</sup> complexes of the salphen ligand (Table 2). It was observed that Mn<sup>II</sup>-salphen was more reactive than either Cu<sup>II</sup> or Fe<sup>II</sup>.

Iron is the most common metal used for treatments of industrial organic wastes and municipal waste waters.<sup>[7,8]</sup> However, the conversion of DMP using Fe<sup>II</sup> catalyst system was less than in case of Mn (Table 2). This could be due to transition of hydrated Fe<sup>II</sup> to a colloidal Fe<sup>III</sup> that catalytically decomposes H<sub>2</sub>O<sub>2</sub> into oxygen and water without forming hydroxyl radicals.<sup>[7,8]</sup> In terms of formation of BQ and DPQ a maximum of 97% BQ formation was obtained with the Cu-based catalyst; the most selective catalyst. When the reaction was carried out with polymer without the metal catalyst no products were observed.

### Effect of H<sub>2</sub>O<sub>2</sub> Concentration

Catalytic oxidation of 2,6-DMP was investigated at three different concentrations of H<sub>2</sub>O<sub>2</sub>, using Cu-salphen supported on PVP-MeI. As the concentration of H<sub>2</sub>O<sub>2</sub> increase the amount of phenol reacted increased and hence, the percent conversion increase (Table 3) where the BQ is major product. However, with increasing the concentration of the H<sub>2</sub>O<sub>2</sub> there may occur build-up of other products that is the DPQ in 21% compared with only 7.2 and 2.6 for Fe<sup>II</sup> and Cu<sup>II</sup>, respectively. No reaction products were obtained in the absence of hydrogen peroxide.

### Effect of pH

The oxidation of 2,6-DMP was studied at pHs 4, 7, and 9 using KH phthalate, phosphate and borate buffers, respectively in the presence of Cu-salphen supported on PVP-MeI (Table 4). The reaction at pH 7 showed maximum conversion of DMP without any effect on the distribution of the reaction products. The reaction at pH 7 using phosphate buffer proceeded in a similar way to previous results obtained for the degradation of

**Table 2.** Oxidation of 2,6-DMP using different metal-salphen catalysts supported on PVP-MeI.<sup>a</sup>

Metal-salphen	% Conversion of DMP	% Selectivity	
		BQ	DPQ
—	0.0	0.0	0.0
Cu-Salphen	47.8	97.4	2.6
Fe <sup>II</sup> -Salphen	62.4	84.5	14.5
Mn <sup>II</sup> -Salphen	68.2	89	11

<sup>a</sup>All reactions were carried out using  $4.6 \times 10^{-4}$  M metal-salphen. Other reaction conditions are given under Table 1.



**Table 3.** Oxidation of 2,6-DMP using different H<sub>2</sub>O<sub>2</sub> concentrations catalyzed by Cu-salphen-supported on PVP-MeI.<sup>a</sup>

Concentration of H <sub>2</sub> O <sub>2</sub> (M)	% Conversion of DMP	% Selectivity	
		BQ	DPQ
—	0.0	0.0	0.0
0.06	47.8	97.4	2.6
0.12	68.4	92.8	7.2
0.24	73	79	21

<sup>a</sup>All reactions were carried out using  $4.6 \times 10^{-4}$  M Cu-salphen,  $4.6 \times 10^{-3}$  M of polymeric pyridinium support,  $6 \times 10^{-2}$  M of

**Table 4.** Oxidation of 2,6-DMP at different pH using Cu-salphen catalyst supported on PVP-MeI.<sup>a</sup>

pH	% Conversion of DMP	% Selectivity	
		BQ	DPQ
9 <sup>b</sup>	47.8	97.4	2.6
7 <sup>c</sup>	58.4	91	9
4 <sup>d</sup>	43	72	28

<sup>a</sup>All reactions were carried out using  $4.6 \times 10^{-4}$  M Cu-salphen,  $4.6 \times 10^{-3}$  M of polymeric pyridinium support,  $6 \times 10^{-2}$  M of 2,6-DMP, and  $6.0 \times 10^{-2}$  M of H<sub>2</sub>O<sub>2</sub>. Reactions were carried out in the presence of 5 mL of buffer solution. The reaction time was 24 h.

<sup>b</sup>Borate buffer.

<sup>c</sup>Phosphate buffer.

<sup>d</sup>KH phthalate.

trichlorophenol with H<sub>2</sub>O<sub>2</sub> catalyzed by iron phthalocyanine.<sup>[18]</sup> However, oxidation of DMP at pH 4 proceeded in slightly lower conversion than at pH 9 but the amount of DPQ was greatly increased compared with pH 7 and 9. Product distribution was greatly affected by the pH decrease, as more DPQ was produced than in the case of pH 7 and 9.

## CONCLUSION

Transition metal-salphen complexes-supported on polyvinylpyridinium salts effectively catalyzed the aqueous oxidation of 2,6-DMP. The PVP-MeI supported Mn-salphen was the most reactive catalyst system while the PVP-BuBr supported Cu-salphen was the most selective catalyst. The catalytic oxidation of 2,6-DMP described in this investigation represents a wastewater purification model that can be applied effectively at industrial sites where such pollutants are produced.





## REFERENCES

1. Vandegrift, G.F.; Reed, D.T.; Tasker, I.R. Eds. *Environmental Remediation: Removing Organic and Metal Ion Pollutants*; ACS Symp. Ser., 1992, Vol. 509; 1.
2. Tuka, V.; Hanika, J. Catalytic wet oxidation of substituted phenols in trickle bed reactor. *J. Chem. Technol. & Biotechnol.* **1989**, *71*, 262.
3. Boyd, S.; Shaobai, S.; Lee, J.-F.; Mortland, M. Pentachlorophenol sorption by organo-clays. *Clays & Clay Min.* **1988**, *63*, 125.
4. Taylor, W.I.; Battersby, A.R. *Oxidative Coupling of Phenols*; Marcel Dekker: New York, 1967.
5. Rivas, J.; Kolackowski, S.T. Hydrogen peroxide promoted wet air oxidation of phenol. *J. Chem. Technol. & Biotechnol.* **1999**, *74*, 390.
6. Hermert, C.; Renz, M.; Meunier, B. Oxidative degradation of chlorinated phenols catalyzed by a non-heme iron (III) complex. *J. Mol. Catal. A: Chemical* **1999**, *137*, 205.
7. Bishop, D.F. Hydrogen peroxide catalytic oxidation of refractory organics in municipal waste waters. *Ind. Eng. Chem., Process Design & Development.* **1968**, *8*, 1110.
8. Walling, C. Fenton's reagent revisited. *Acc. Chem. Res.* **1975**, *8*, 125.
9. Sherrington, D.C.; Hodge, P. *Synthesis and Separations Using Functional Polymers*; Wiley: New York, 1988.
10. Ford, W.T. Ed. *Polymeric Reagents and Catalysts*; ACS Symp. Ser., 1986; Vol. 308.
11. Gates, B.C. *Catalytic Chemistry*; Wiley: New York, 1992.
12. Chanda, M.; O'Driscoll, K.F.; Rempel, G.L. Sorption of phenols onto crosslinked poly(4-vinylpyridine). *React. Polym.* **1983**, *1*, 281.
13. Kawabata, N.; Ohira, K. Removal and recovery of organic pollutants from aquatic environment. Vinylpyridine-divinylbenzene copolymer as a copolymeric adsorbent for removal and recovery of phenol from aqueous solutions. *Environ. Sci. Technol.* **1979**, *13*, 1396.
14. Tadokoro, H.; Tsuruya, S. Catalysis of poyvinylpyridine-supported Cu (II) during 2, 6-di-*t*-butylphenol oxidation in presence of inorganic bases. *J. Catal.* **1992**, *138*, 24.
15. Berry, K.; Moya, F.; Murray, K.S.; Van den Bergen, A.M.B.; West, B. Water-soluble complexes of *bis*-salicylaldimine-5-sulfonic acids. Oxygen carrying properties and conversion into cobalt (III) organometallic compounds. *J. Chem. Soc. Dalton Trans.* **1982**, 109.
16. *Vogel's Textbook of Quantitative Inorganic Analysis*, 4th Ed.; Longman, 1978.
17. El-Hamshary, H.; El-Garawany, M.; Assubaie, F.; Al-Eed, M. Synthesis of poly(acrylamide-*co*-4-vinylpyridine) hydrogels and their application in heavy metal removal. *J. Appl. Polym. Sci.* **2003**, *89*, 2522.
18. Sanchez, M.; Meunier, B. Key role of the phosphate buffer in the H<sub>2</sub>O<sub>2</sub> oxidation of aromatic pollutants catalyzed by iron tetrasulfophthalocyanine. *J. Catal.* **2000**, *202*, 177.

Received July 2003

Accepted August 2003

