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FORMATION OF VANILLIN AND VANILLIC ACID FROM KRAFT LIGNIN THROUGH GREEN CHEMICAL OXIDATION

(Pembentukan Vanillin dan Asid Vanillik dari Kraft Lignin melalui Proses Pengoksidaan Kimia Hijau)

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Abstract

The development of efficient methods to produce useful small molecules such as vanillin and vanillic acid from kraft lignin is an important goal for a sustainable production of fine chemicals. It is generally known that oxidative treatments of kraft lignin can cause partial oxidative depolymerization to produce vanillin, but the conditions required are usually harsh and the yields are low. Therefore, the possibility of achieving the same reaction at 25 °C using an alternative green chemical catalytic oxidation process involving hydrogen peroxide and an Fe(TAML$^{®}$) oxidation catalyst was investigated. Preliminary experiments using this method at 25 °C with kraft lignin resulted in the formation of small amounts of vanillin (ca. 5%) as well as vanillic acid (<1%). The influence of key parameters including the concentrations of the catalyst (2.0-4.0 µM) and H_2O_2 (0.5-2.0 mM) on the amount of these compounds formed were reported.

Keywords: Fe(TAML$^{®}$), hydrogen peroxide, kraft lignin, vanillin, vanillic acid

Abstrak

Pembangunan kaedah yang berkesan untuk menghasilkan molekul kecil yang berguna seperti vanillin dan asid vanillik dari kraft lignin adalah penting bagi penghasilan bahan kimia yang mampan. Adalah diketahui bahawa pengoksidaan kraft lignin mampu mengakibatkan depolimerisasi oksidatif separa untuk memberikan vanilin, tetapi kondisi yang diperlukan biasanya kasar dan hasilnya rendah. Oleh itu, kemungkinan untuk mencapai tindak balas yang sama pada 25 °C menggunakan proses pengoksidaan pemangkin kimia alternatif yang melibatkan hidrogen peroksida dan pemangkin pengoksidaan Fe (TAML®) disiasat. Eksperimen awal menggunakan kaedah ini pada 25 °C dengan kraft lignin mengakibatkan pembentukan sejumlah kecil vanillin (sekitar 5%) serta asid vanillik(<1%). Pengaruh parameter utama termasuk kepekatan pemangkin (2.0-4.0 µM) dan H_2O_2 (0.5-2.0 mM), keatas jumlah pembentukan sebatian ini dilaporkan.

Kata kunci: Fe(TAML$^{®}$), hidrogen peroksida, kraft lignin, vanillin, asid vanillik

Introduction

There is an increasing worldwide drive to develop sustainable alternatives in the use of fossil carbon (coal, oil and gas) as fuels and feedstock for the chemical industry. Lignin is the second-most abundant renewable polymer on earth next to cellulose and can contribute up to 30% of the weight of lignocellulosic biomass. Furthermore, lignin represents one of the very few abundant natural resources that, in principle, could serve as a renewable source of small aromatic building blocks for other more complex organic molecules [1 – 4]. However, the production of smaller organic molecules from lignin is generally hampered by the nature of lignin as an insoluble, complex three-dimensional amorphous polymer, which is formed by the radical polymerization of three types of hydroxycinnamyl alcohol precursors (*p*-coumaryl, coniferyl, and sinapyl alcohols) known as monolignols, and the resulting polymer contains numerous types of ether (C-O-C) as well as carbon-carbon (C-C) linkages that connect the monomer units. Therefore, unlike many other polymers, lignin does not have a simple repeating chemical structure. Furthermore, many connecting groups are not easily cleaved. Consequently, it is very difficult to obtain high yield of simple, useful organic molecules through the depolymerization of lignin [2].

Kraft lignin, on the other hand, is lignin that has been partially broken down and solubilized. It is produced during the pulping of wood to obtain cellulose fibers for making paper. Globally, more than 72 million tons of kraft lignin are annually produced this way. During kraft pulping, strong alkali and sulfide solution at high temperatures partially break down and solubilize the lignin. After removing the cellulose by filtration, the highly modified, soluble kraft lignin is usually burnt in the recovery boiler to produce heat. However, it has long been recognized that the enormous amounts of kraft lignin produced this way could be much better utilized if an efficient method is found to break it down into small molecules that either were of intrinsic commercial value or could be used as platform compounds for producing fine chemicals [5, 6].

Numerous methods for the depolymerization of kraft lignin to produce fine chemicals have been investigated including hydrolysis, reduction, oxidation and pyrolysis. Among these, oxidation has been the most studied as it tends to give better yield of usefully functionalized molecules. Oxygen is by far the most common oxidant that has been utilized although high temperatures and high oxygen pressures are needed to obtain moderate yield of aromatic compounds [7, 8]. Remarkably, there are very few studies in which hydrogen peroxide has been used for the oxidative depolymerization of kraft lignin [9]. Notably, it has been reported that in the presence of catalytic amounts of simple transition metal salts namely $MnSO_4$, $FeSO_4$ or Na_2WO_4, very small amounts of aromatic compounds including vanillin can be produced on treatment with hydrogen peroxide under mild conditions, but the yields are ≤ 0.51 wt.% [7].

This study has a long-standing interest in the use of the Fe(TAML®) complex, FeB* (see Figure 1) to catalyze the H_2O_2 bleaching (oxidation) of residual lignin on cellulose fibers obtained from the kraft pulping process [10 – 13]. The use of hydrogen peroxide as the oxidant for this purpose is particularly attractive as it is readily available, inexpensive and unlike chlorine-based bleaches, it does not form organo-chlorine by-products, which led this study to consider whether or not the same catalytic oxidation system could be adapted to oxidatively depolymerize kraft lignin and produce aromatic compounds like vanillin under mild conditions if very limited amounts of hydrogen peroxide were employed. The oxidation catalyst, FeB*, is non-toxic and comprises elements commonly found in the biological systems. It is water-soluble and is a very potent and efficient activator of hydrogen peroxide, even at nanomolar concentrations [14, 15]. When the catalyst is eventually degraded, it is transformed into environmentally benign byproducts. Importantly, the hydrogen peroxide oxidation of organic compounds catalyzed by FeB* occurred rapidly at 25 °C [14, 15]. In this paper, a small amount of vanillin (up to 5%) as well as vanillic acid (ca. 1%) was observed upon the treatment of kraft lignin with the FeB*/H_2O_2 system at 25 °C. The results showed that partial depolymerization of kraft lignin occurred under these conditions. The influence of key parameters such as the concentrations of the catalyst and H_2O_2, on the amounts of these compounds formed was also presented.

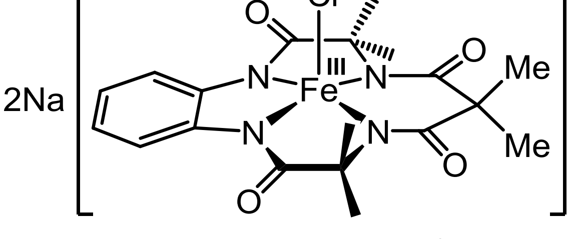

Figure 1. Molecular structure of the Fe(TAML®) compound FeB*

Materials and Methods

Generals procedures

All chemical reagents were analytical grade and used without purification. Softwood kraft lignin samples were obtained from Sigma Aldrich (37,095-9) (SAKL) while hardwood kraft lignin was obtained from Scion Ltd. NZ (*Eucalyptus regnans*) (SCKL). The iron TAML catalyst FeB* was collected from GreenOx Catalysts, Inc. 4400 Fifth Ave, Suite 713 Pittsburgh, PA 15213, USA and used without further purification. The effective M_r of 667.32 g mol^{-1} supplied by the manufacturer was used to calculate catalyst concentrations of the solutions prepared. The catalyst solutions were prepared in deionized water and used within three days. Meanwhile, the $Na_2CO_3/NaHCO_3$ buffer solutions (pH 9.5, 0.010 mol L^{-1}) were prepared using a standard literature procedure [16]. The pH of each buffer solution prepared was checked using a Sartorius PB-10 pH meter fitted with a Sartorius pH/ATC electrode. Hydrogen peroxide stock solutions were made by diluting a commercial solution (~30% w/v) to approximately 1% w/v with deionised water. The solutions were then standardized by UV-Vis absorbance measurement in quartz cuvette cells at 230 nm using $\varepsilon = 72.8$ mol^{-1} L cm^{-1} [17]. UV-Vis measurements were made using a double beam Perkin Elmer Lamda 35 UV-Visible spectrophotometer with a slit width of 1.0 nm and a scan speed of 480 nm/min. Concentrations were determined from the average of three triplicate measurements. The results were confirmed by titration with standard thiosulphate solution (ca. 0.1M concentration accurately determined by iodometric titration [18].

To prepare the standard calibration curves for the analysis of both vanillin and vanillic acid by HPLC, a set of solutions of pure compounds with concentrations of 1.00×10^{-5}, 3.00×10^{-5}, 6.00×10^{-5}, 9.00×10^{-5} and 1.20×10^{-4} mol L^{-1} were prepared in $Na_2CO_3/NaHCO_3$ buffer solution (pH 9.5, 0.010 mol L^{-1}). To an aliquot (10.0 mL) of each solution, acetic acid (1.50 mL of 0.10 mol L^{-1} solution) was added to reduce the pH to ~5.5. After filtration through a small membrane filter, the resulting solution was analyzed by HPLC (injection volume 100 µL, UV-Vis detector set at 270 nm) using the same conditions detailed below for analyzing the lignin samples.

Lignin oxidative depolymerization reactions

In this typical experiment with the temperature maintained at 25 °C, a sample of lignin (12.5 mg) was placed in a 100 mL beaker and $Na_2CO_3/NaHCO_3$ buffer solution (40 mL of a 0.010 mol L^{-1} solution, pH 9.5) was added. While stirring with a magnetic stir bar, aliquots of standard FeB* solution and standard H_2O_2 solution were then added so that the overall concentrations of FeB* and H_2O_2 would be 2.00 µM and 1.00 mM, respectively, once the total solution volume had reached 50 mL by the addition of more buffer solution. The additional buffer solution was added as soon as possible after the adding the FeB* and H_2O_2. The resulting mixture (50 mL) was then stirred at 25 °C for 1 hour. After this time, catalase was added to destroy the remaining hydrogen peroxide and stop the reaction. After one hour, the solution was checked with a peroxide test strip to confirm that all the hydrogen peroxides have been destroyed. An aliquot (10.0 mL) of the solution was removed and acetic acid (1.50 mL of 0.10 mol L^{-1} solution) was added to acidify the solution to pH ~5.5. After filtration through a small membrane filter of 0.4 nm, the resulting solution was analyzed by HPLC using the conditions detailed below. Experiments were carried out using the two different lignins (SAKL and SCKL) with different concentrations of FeB* and hydrogen peroxide.

HPLC analysis

Measurements were made on a Shimadzu LC-20AT HPLC with an SPL-20A UV-Vis detector. The column used was a ProntoSIL EPS column-W RP C18 reverse-phase HPLC column (25 x 0.46 cm, 10 µm). The column temperature was 25 °C, while the diode array detector was set to measure absorbance at 270 with a flow rate of 1.0 mL/min and injection volume of 100 µL. The mobile phases were; Solvent A comprising milli-Q water acidified with 1.25% (v/v) acetic acid and Solvent B that contains pure methanol. Samples were eluted using the following conditions; t = 0, Solvent A 95%; t = 5 min, Solvent A 90% (linear gradient); t = 10 minutes, Solvent A 90% (isocratic); t = 40 minutes, Solvent A 65% (linear gradient); t = 50 minutes Solvent A 65% (isocratic). Between each analysis, the column was eluted with Solvent B (100%) for 15 minutes followed by elution with Solvent A (95%) for 5 minutes [19].

Results and Discussion

The production of vanillin and vanillic acid from Kraft lignin through a catalytic oxidative treatment at 25°C was investigated. The formation of these two products was studied since preliminary experiments indicated that they were the major water-soluble products formed under the conditions used. The catalytic oxidation system employed was hydrogen peroxide in the presence of FeB* at 25 °C in alkaline (pH 9.5) solution. The rates at which FeB* catalyzes hydrogen peroxide oxidations of organic substrates were very rapid at 25 °C in the basic solution and reached a maximum at pH *ca.*10.8. At pH 9.5, the rates of oxidation were slower by more than an order of magnitude. Since it was anticipated that catalytic oxidation and/or polymerization of the vanillin produced could occur in unwanted side-reactions, this study opted to carry out the reactions at this lower pH to minimize the rates of these reactions. In a further attempt to limit unwanted oxidation of the products, this study also restricted the amount of hydrogen peroxide used to 1.36 mg per 10.0 mg lignin. There have been no previous reports on the use of this catalytic oxidation system for vanillin and vanillic acid production from kraft lignin.

In the blank reactions in which neither hydrogen peroxide nor the FeB* catalyst was present, only a very small amount of vanillin was obtained from each kraft lignin (Entry 1, Table 1). The other two blank reactions in which only the FeB* catalyst or only hydrogen peroxide was added (entries 2 and 3, Table 1) provided some unexpected results. In the reactions to which only FeB* (4.00 µM) was added (entry 2, Table 1), the amount of vanillin produced from the SCKL lignin had increased from 0.46% to 1.47% (a factor of 3.2). For the SAKL lignin, an increase was also observed, which was much smaller from 0.87% to 1.07% (a factor of 1.23). There was no clear evidence as to why the increased amounts of vanillin were produced in both cases. However, one possibility is that FeB* had utilized atmospheric oxygen as an oxidant for these reactions. Oxidation reactions using oxygen and the catalyst FeB* have been reported previously [20]. The other blank reactions in which the kraft lignin samples were stirred in alkaline buffer with hydrogen peroxide alone at 20 °C resulted in unexpectedly large amounts of vanillin formed (Entry 3, Table 1). Under these conditions, similar amounts (5.19% and 5.48%) of vanillin were obtained from both lignin samples.

The reaction of the two kraft lignins with hydrogen peroxide and catalyst FeB* (entries 4-7, Table 1) produced vanillin, but the amounts varied considerably depending on the amounts of hydrogen peroxide and catalyst used. In all cases, the amounts of vanillin were less than 1%, except for Entry 6 in which the concentrations of FeB* and H_2O_2 were 4.00 µM and 1.00 mM, respectively. With the SCKL lignin, a considerable amount of vanillin (4.27%) was produced, which was slightly less than the amount formed by hydrogen peroxide alone (5.18%). However, for the SAKL lignin, the results were very different. Although this ratio also produced the largest amount of vanillin from all the FeB*/H_2O_2 reactions (entries 4-7, Table 1), the amount was only 1.07%, which was considerably less than the amount formed by hydrogen peroxide alone (5.48%). Again, this underscores how differently sourced kraft lignins can display very different reactivity.

Table 1. Formation of vanillin from SCKL and SAKL kraft lignins after treatment with different concentrations of hydrogen peroxide and the oxidation catalyst FeB* at 25 °C and pH 9.5 for one hour

Entry Number	**Concentrations of Reagents**		**Kraft Lignin Source**			
			SCKL		**SAKL**	
	[FeB*] (µM)	**[H_2O_2] (mM)**	**[Vanillin] (mg/L)**	**% Vanillin (by wt.)**	**[Vanillin] (mg/L)**	**% Vanillin (by wt.)**
1	0	0	1.15	0.46	2.18	0.87
2	4.00	0	3.67	1.47	2.68	1.07
3	0	1.00	13.0	5.19	13.7	5.48
4	2.00	1.00	1.67	0.67	0.51	0.22
5	2.00	2.00	1.81	0.72	1.59	0.64
6	4.00	1.00	10.7	4.27	2.67	1.07
7	4.00	0.50	1.75	0.70	1.01	0.40

The amounts of vanillic acid formed during each of the oxidative reactions are presented in Table 2. In each case, the amounts of vanillic acid were much less than the amounts of vanillin obtained. Interestingly, the same conditions that produced the largest amounts of vanillin also produced the largest amounts of vanillic acid. Thus, upon treatment with hydrogen peroxide alone (Entry 3, Table 2) 0.46% and 0.75% of vanillic acid were obtained from the SCKL and SAKL lignins, respectively. For the other two blank reactions (entries 1 and 2, Table 2) relatively larger amounts of vanillic acid were formed from the SAKL lignin than that of the SCKL lignin. In all cases, the FeB*/H_2O_2 oxidation system produced less vanillic acid than the amount obtained using hydrogen peroxide alone (entries 4-7, Table 2). For the FeB* catalyzed reactions, it was again when the concentrations of FeB* and H_2O_2 were 4.00 µM and 1.00 mM, respectively, that the maximum amount of vanillic acid was formed (Entry 6, Table 2).

Table 2. Formation of vanillic acid from SCKL and SAKL kraft lignins after treatment with different concentrations of hydrogen peroxide and the oxidation catalyst FeB* at 25 °C and pH 9.5 for one hour

Entry Number	**Concentrations of Reagents**		**Kraft Lignin Source**			
			SCKL		**SAKL**	
	[FeB*] (µM)	**[H_2O_2] (mM)**	**[Vanillic Acid] (mg/L)**	**% Vanillic Acid (by wt.)**	**[Vanillic acid] (mg/L)**	**% Vanillic Acid (by wt.)**
1	0	0	0.05	0.02	0.86	0.34
2	4.00	0	0.40	0.16	1.30	0.52
3	0	1.00	1.15	0.46	1.88	0.75
4	2.00	1.00	0.15	0.06	0.12	0.05
5	2.00	2.00	0.04	0.01	0.53	0.21
6	4.00	1.00	0.79	0.32	0.68	0.27
7	4.00	0.50	0.18	0.07	0.32	0.13

Meanwhile, the SCKL lignin started to approach the amount of vanillic acid formed by hydrogen peroxide alone (0.32% vs 0.46%), whereas it was considerably less in the case of the SAKL lignin (0.27% vs 0.75%). The results in tables 1 and 2 provide no evidence that catalytic oxidation of vanillin produced vanillic acid. Thus, although relatively small amounts of vanillin were obtained from the catalytic reactions as represented in entries 4, 5 and 7 of Table 1, there were no corresponding increase in vanillic acid formation under these same conditions (Table 2). Besides, although considerably more vanillin was formed from the SCKL lignin (4.27%) than the SAKL lignin (1.07%) (Entry 6 Table 1), almost the same amount of vanillic acid (0.32 and 0.27%, respectively) was formed in each case under these conditions (Entry 6, Table 2). A possible further complication is that the FeB*/H_2O_2 system could initiate some oxidative polymerization of several formed vanillin and/or vanillic acid. It was shown that this catalytic system can cause the oligomerization/polymerization of phenolic compounds including bisphenol A [21].

Conclusion

The treatment of kraft lignins with the FeB*/H_2O_2 catalytic oxidation system at 25 °C for one hour has resulted in oxidative depolymerization to form small amounts of vanillin (up to 4.27%) and vanillic acid (up to 0.32%). The amounts of these products formed were highly dependent on the source of the kraft lignin and the conditions used. Surprisingly, it has been found that the treatment of these kraft lignins with hydrogen peroxide alone under the same mild conditions resulted in the formation of slightly more of each of these two products (5.48% and 0.75%, respectively). It is possible that during the FeB*/H_2O_2 oxidation reactions, competing non-productive oxidations utilized some of the hydrogen peroxide and therefore reducing the amount of vanillin and vanillic acid produced. Furthermore, oxidative polymerization of vanillin and vanillic acid may also occur under these conditions, which further reduced the yield of these compounds. The amounts of vanillin obtained by these hydrogen peroxide oxidative depolymerization reactions all fall within the range (3.5 – 10% by weight) previously reported for different kraft lignins upon the treatment with oxygen (9 bar) at 130-150 °C for several hours. Further refinement of the oxidative reactions described in this study could therefore lead to a more efficient method of vanillin production from kraft lignin. The intriguing observation was that the treatment of kraft lignin with FeB* under aerobic conditions had produced some vanillin and vanillic acid, which also merits further investigation.

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References

1. Mahmood, N., Yuan, Z., Schmidt, J. and Xu, C. C. (2016). Depolymerization of lignins and their applications for the preparation of polyols and rigid polyurethane foams: A review. *Renewable and Sustainable Energy Reviews*, 60: 317-329.
2. Lange, H., Decina, S. and Crestini, C. (2013). Oxidative upgrade of lignin–Recent routes reviewed. *European Polymer Journal*, 49(6): 1151-1173.
3. Zakzeski, J., Bruijnincx, P. C., Jongerius, A. L., & Weckhuysen, B. M. (2010). The catalytic valorization of lignin for the production of renewable chemicals. *Chemical Reviews*, 110(6): 3552-3599.
4. Bjørsvik, H. R. and Liguori, L. (2002). Organic processes to pharmaceutical chemicals based on fine chemicals from lignosulfonates. *Organic Process Research & Development*, 6(3): 279-290.
5. Pinto, P. C. R., Costa, C. E. and Rodrigues, A. E. (2013). Oxidation of lignin from *Eucalyptus globulus* pulping liquors to produce syringaldehyde and vanillin. *Industrial & Engineering Chemistry Research*, 52(12): 4421-4428.
6. Voitl, T. and Rohr, P. R. V. (2009). Demonstration of a process for the conversion of kraft lignin into vanillin and methyl vanillate by acidic oxidation in aqueous methanol. *Industrial & Engineering Chemistry Research*, 49(2): 520-525.
7. Napoly, F., Kardos, N., Jean-Gérard, L., Goux-Henry, C., Andrioletti, B. and Draye, M. (2015). H_2O_2-mediated kraft lignin oxidation with readily available metal salts: What about the effect of ultrasound?. *Industrial & Engineering Chemistry Research*, 54(22): 6046-6051.
8. Voitl, T., Nagel, M. V. and von Rohr, P. R. (2010). Analysis of products from the oxidation of technical lignins by oxygen and H3PMo12O40 in water and aqueous methanol by size-exclusion chromatography. *Holzforschung*, 64(1): 13-19.
9. Ouyang, X., Ruan, T. and Qiu, X. (2016). Effect of solvent on hydrothermal oxidation depolymerization of lignin for the production of monophenolic compounds. *Fuel Processing Technology*, 144: 181-185.
10. Wingate, K. G., Stuthridge, T. R., Wright, L. J., Horwitz, C. P. and Collins, T. J. (2004). Application of TAML® catalysts to remove colour from pulp and paper mill effluents. *Water Science and Technology*, 49(4): 255-260.
11. Horwitz, C. P., Collins, T. J., Spatz, J., Smith, H. J., Wright, L. J., Stuthridge, T. R., Wingate, K. G & McGrouther, K. (2006). Iron-TAML® catalysts in the pulp and paper industry. *ACS Symposium Series*, 921: 156-169
12. Collins, T. J., Horwitz, C. P., Ryabov, A. D., Vuocolo, L. D., Gupta, S. S., Ghosh, A., Fattaleh, N. L., Handgun, Y., Steinhoff, B., Noser, C. A. and Beach, E. (2002). Tetraamido macrocyclic ligand catalytic oxidant activators in the pulp and paper industry. *Advancing Sustainability through Green Chemistry and Engineering*, 823: 47-60.
13. Collins, T. J., Hall, J. A., Vuocolo, L. D., Fattaleh, N. L., Suckling, I., Horwitz, C. P., Gordon-Wylie, S. W., Allison, R. W. Fullerton, T. J., Wright, L. J., (2000). The activation of hydrogen peroxide for selective, e. w. p. b.; In "Green Chemistry: Challenging Perspectives P. T., ed., Oxford University Press, Oxford, pp. 79-105
14. Bartos, M. J., Gordon-Wylie, S. W., Fox, B. G., Wright, L. J., Weintraub, S. T., Kauffmann, K. E., Münck, E., Kostka, K.L., Uffelman, E.S., Rickard, C.E. and Noon, K. R. (1998). Designing ligands to achieve robust oxidation catalysts. Iron based systems. *Coordination Chemistry Reviews*, 174(1): 361-390.
15. Ryabov, A. D. and Collins, T. J. (2009). Mechanistic considerations on the reactivity of green FeIII-TAML activators of peroxides. *Advances in Inorganic Chemistry*, 61: 471-521.

16. Delory, G. E. and King, E. J. (1945). A sodium carbonate-bicarbonate buffer for alkaline phosphatases. *Biochemical Journal*, 39(3): 245.
17. Chahbane, N., Popescu, D. L., Mitchell, D. A., Chanda, A., Lenoir, D., Ryabov, A. D., Schramm, K.W. and Collins, T. J. (2007). Fe III–TAML-catalyzed green oxidative degradation of the azo dye Orange II by H_2O_2 and organic peroxides: products, toxicity, kinetics, and mechanisms. *Green Chemistry*, 9(1): 49-57.
18. Kingzett, C. T. (1888). On the estimation of peroxide of hydrogen. *Analyst*, 13: 62-63.
19. Voisine, R., Carmichael, L., Chalier, P., Cormier, F. and Morin, A. (1995). Determination of glucovanillin and vanillin in cured vanilla pods. *Journal of Agricultural and Food Chemistry*, 43(10): 2658-2661.
20. Tang, L. L., Gunderson, W. A., Weitz, A. C., Hendrich, M. P., Ryabov, A. D. and Collins, T. J. (2015). Activation of dioxygen by a TAML activator in reverse Micelles: characterization of an $Fe^{III}Fe^{IV}$ dimer and associated catalytic chemistry. *Journal of the American Chemical Society*, 137(30): 9704-9715.
21. Onundi, Y., Drake, B. A., Malecky, R. T., DeNardo, M. A., Mills, M. R., Kundu, S. and Truong, L. (2017). A multidisciplinary investigation of the technical and environmental performances of TAML/peroxide elimination of Bisphenol A compounds from water. *Green Chemistry*, 19(18): 4234-4262.