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UV-induced colour generation of pulp and paper mill effluents as a proxy of ligno-cellulosic biorefinery wastewater

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ABSTRACT

UV-induced colour generation of treated (clear) wastewater effluents from a modern bisulphite pulp and paper mill was investigated as a model for aqueous discharges likely to be encountered with emerging biorefinery concepts. Aqueous solutions of selected model compounds, namely lignosulfonic acid (LSA), humic acid and vanillin were exposed to UV light and the colour generation of these solutions compared to the industrial effluent. The colour generation trend of the wastewater was found to be similar to that of LSA. Analysis by HPLC, FTIR, MS and NMR showed that the colour development of the wastewater mimicked the paper yellowing mechanism, with the formation of quinones as a major route. UV-induced dimerization of vanillin solutions showed a dramatic increase in colour. Thus results suggest the UV induced polymerization of lignin compounds play a major role in colour development of lignocellulosic wastewater effluents unless the phenol precursors are removed or degraded.

1. Introduction

The transformation of ligno-cellulosic biomass into a combination of biofuels, green chemicals and materials is currently very topical [1–5]. Accordingly, a consideration of the expected aqueous discharge associated with integrated forest biorefinery process strategies is crucial. The biorefinery concept highlights sustainability, climate change mitigation and low carbon footprint, and hence the development of water treatment systems that are equally environmentally friendly is correspondingly important.

The utilization of ligno-cellulosic biomass in both bioenergy and biomaterial production is commonly conducted via an initial biomass pretreament to overcome the recalcitrance of the lignin-hemicellulose matrix so as to solubilize and degrade it, providing access for subsequent processing [6–8]. The strategies typically include steam explosion, dilute acid and organosolv pretreatment, usually performed under elevated temperature and strong shear (pressure or mechanical). Amongst these, acid-catalyzed or auto-catalyzed processes are becoming dominant pretreatment strategies for the biorefinery.

One problem regarding wastewater streams that have originated from wood/lignocellulosic processing is the persistent colour of the treated effluent [9–12]. Additionally, there is a concern regarding further yellowing of the treated wastewater that may occur and intensify beyond the point of discharge, even after prolonged time periods. This study aimed to investigate the mechanism of UV-induced colour generation associated with wastewater from the acidic (bisulphite) pulping process, considered in the context of prospective integrated forest biorefineries.

Components of biorefinery effluents that are believed responsible for the colour include residual cellulose, hemicelluloses, lignin, pulping process chemicals and microorganism from the wastewater stream. Oxidative reactions of these components may result in coloured degradation products, usually containing carbonyl (C=O) groups and carbon-carbon double bonds (C=C) [10,13,14]. Among those, lignin residues have often been linked to effluent colour development [15,16]; however, evidence is scarce, and even more scarce concerning the governing mechanisms.

Successful methods for colour removal from pulp and paper mill effluents [17–24] have been reported. These include physicochemical treatment, biological treatment and integrated treatments which combine two or more processes [25–27]. Physicochemical treatments, such as coagulation [18,23], electrocoagulation [17,28,29], and adsorption [19,24] can remove up to 90% of colour from the effluents. Biological treatment with algae can successfully remove 84% of the colour from a pulp and paper industry effluent [30]. Combining coagulation-flocculation with heterogeneous photocatalysis (a $UV/TiO_2/H_2O_2$ process)

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was reported to remove 100% of the chromophores absorbing at 500 nm [20].

However, most studies have focused on the removal of colour from the effluents, not on the identification of substances responsible for the stable colour of the effluents or on the mechanism of colour generation. Additionally, the fate of colour from pulp and paper mill effluent and the kinetics of UV-induced colour generation of the treated wastewater have remained unknown. Improved understanding surrounding the colour-producing species as well as the mechanism and rate of colour development in aqueous discharges would be invaluable for the development of robust water treatment process water, especially in the context of emerging biorefineries.

We raise the hypothesis that the colour generation mechanism of pulp mill wastewater is similar to that of the well-established high yield pulp paper yellowing. Light-induced yellowing of paper has been studied both on lignocellulosics fiber made paper and on model compounds. The behaviour of the active chromophores and intermediates was characterized and precise reaction pathways of the participating species during irradiation were validated [31,32]. Factors contributing to the oxidation reactions are light, heat, moisture, metal cations (Cu^{2+} and Fe^{3+}) and pollutant gases (SO_2 and NO_2). The discolouration of paper is initiated by photooxidation upon light absorption by some chromophores present in paper. Lignin reactions were identified as the major cause of photo yellowing [33,34]. Therefore, lignin and depolymerised lignin derivatives are hypothesised to be responsible for the colour development in pulp and paper mills wastewater even long after treatment [10].

In this study, the effluent from an integrated magnesium bisulphite pulp mill was investigated as a model for aqueous discharge from lignocellulosic biorefineries. The bisulphite pulping process is acidic, similar to the stream explosion based wood treatments of chemical based enzymatic and fermentation based biorefineries. In the first part of this study, the UV-induced colour growth rate of the effluent was determined and compared to three model substances, namely vanillin, lignosulfonic acid (LSA) and humic acid. These model substances represent a simple lignin fragment (vanillin), a bisulphite pulping byproduct (LSA), and a more complex material of combined aliphatic-aromatic composition (humic acid). These model substances are all water soluble. In the second part, the composition of aqueous solutions and UV-irradiation products were investigated using High Performance Liquid Chromatography (HPLC) and spectroscopic analysis. Finally, the mechanism of colour generation is analysed from the results of lignin model compounds reactions that have been analysed by Nuclear Magnetic Resonance (^{1}H-NMR), Electrospray Mass Spectrometry (ES-MS) and Fourier Transform Infrared Spectroscopy (FTIR) analyses.

2. Experimental

2.1. Materials

The wastewater used in this study was the treated effluent from the Kimberly Clark Australia (KCA) Tantanoola pulp and paper mill located at Snuggery in South East South Australia. The Tantanoola pulp mill, now closed, produced 70 kt y^{-1} of magnefite chemical pulp and its water usage was about 60 $m^3\,t^{-1}$ of pulp. The logs were debarked before chipping. The feedstock consisted of Pinus radiata aged 12 to 15 years that was seasoned for 3 months, magnesium oxide (with less than 2.5% of calcium) and molten sulphur. The magnesium bisulphate process was carried out at pH 4.5, 170 °C and for 6 h of batch cooking.

The effluent from four tissue machines was combined with those of the pulp mill. The mill wastewater treatment plant consisted of two primary sedimentation clarifiers and three aerated stabilized basins in series for secondary treatment, before discharge into a nearby lake [35]. The basic properties of the wastewater are provided in Table 1.

Aqueous solutions of LSA (200 ppm), humic acid (50 ppm) and vanillin (250 ppm) were also studied for UV-induced colour generation.

Table 1
Properties of the wastewater.

Property	Effluent
Colour (PtCo)	151
pH	6.9
Total Phosphorus (mg/L)	0.54
TOC (mg/L)	118

The concentrations of LSA and humic acid were adjusted so that the colour levels (measured as PtCo) were approximately similar to that of the wastewater, with vanillin an exception due to its colourless nature. All model compounds were purchased from Sigma Aldrich Pty. Ltd., Sydney, Australia. The LSA was lignosulfonic acid sodium salt having a weight average molecular weight (Mw) of 52,000 and number average molecular weight (Mn) of 70,000. The pH of all model compound solutions was in the range 6-7. The exact chemical structure of humic acid is unknown: however, several models of humic acid have been reported, one of which was suggested by Steelink [36].

2.2. Methods

A small volume of the sample solution (5 ml) was placed in a capped quartz container with diameter of 12 mm and length of 80 mm. The UV irradiation experiments were performed using an Ultraviolet Products CL1000(M/S) UV-crosslinker lamp (302 nm and 254 nm) as described by Johnston [37]. The CL1000 M crosslinker lamp produced mid-range UV wavelength centred at 302 nm and the CL1000S UV crosslinker lamp produced shortwave 254 nm with irradiation intensity 0.28 J $cm^{-2}\,s^{-1}$.

The initial and irradiated aqueous solutions were then analysed using an HACH DR5000 spectrophotometer for colour (PtCo) according to method number 8025 adapted from Hongve and Åkesson [38] and for UV-absorbance over the range 250–650 nm. To investigate the changes in composition due to irradiation, reverse phase High Performance Liquid Chromatography (HPLC) using an Alphabond Phenyl (SN 97,061,184) column (4.6 x 300 mm) and an isocratic mobile phase, acetonitrile and water (40:60, v/v), with a flow rate of 0.8 $cm^3\,min^{-1}$. For vanillin, the resulting compounds after irradiation were also analysed by mass spectrometry (Agilent ESI-MS) and proton nuclear magnetic resonance (^{1}H-NMR, Bruker 400 MHz DRX) using D_2O as solvent.

3. Results and discussion

The colour generation of the magnesium bisulphite pulp mill wastewater and aqueous solutions of the model compounds, LSA, vanillin, and humic acid, was studied under UV illumination at two wavelengths, 254 nm and 302 nm. In the first part of this study, the effects of UV wavelength and irradiation time on colour generation are quantified in terms of colour wavelength and intensity. In the second, the chemical changes attributed to the colour generation are investigated using HPLC, FTIR, MS and NMR.

3.1. Effect of irradiation wavelength and time

Wastewater, together with the humic acid, LSA, and vanillin model solutions were irradiated with UV at two wavelengths (254 nm and 302 nm) for different periods. The colour development (as PtCo) was measured as a function of irradiation time. The plots of colour versus irradiation time for vanillin, LSA, humic acid and wastewater solutions are illustrated in Fig. 1(a–d).

After 1 h stabilization period, the colour intensity for vanillin, LSA, and wastewater solutions all increase pseudo-linearly with irradiation time. The slope of each plot represents the rate constant for colour growth in aqueous solution. Rate constants for vanillin, LSA and

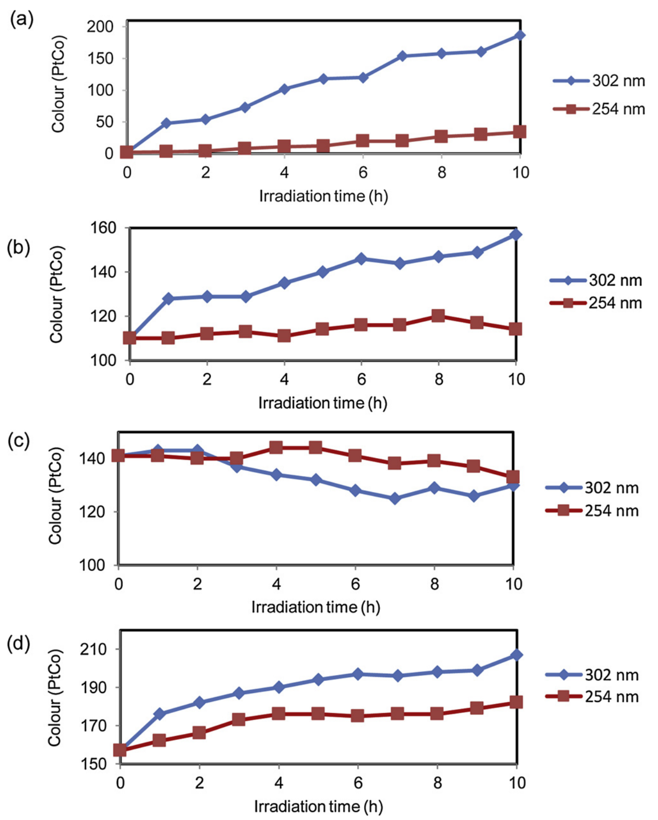

Fig. 1. Colour development in (a) vanillin solution, (b) LSA solution, (c) humic acid solution and (d) wastewater process water upon UV irradiation. Two wavelengths were investigated: 254 nm and 302 nm.

wastewater solution were determined to be: 15.7 PtCo h^{-1}, 2.98 PtCo h^{-1} and 2.87 PtCo h^{-1}, respectively (at 302 nm irradiation). The rate constants for all samples at 254 nm were lower than at 302 nm.

For vanillin, the 254 nm and 302 nm colour growth rates were significantly higher than those of the wastewater and LSA solutions. The initial vanillin solution is colourless and the development of a yellow colour is easily observed as the solution is irradiated. The yellowing rate at 302 nm of vanillin solutions was five times faster than for the LSA and wastewater solutions. This is due to the high concentration of chromophoric entities in the vanillin structure generating a more pronounced colour generation. The low molecular weight of vanillin, compared to LSA, presumably leads to higher diffusion in solution and hence, more effective collisions, allowing more efficient photochemical reaction to occur.

For LSA, colour generation is expected to be due to the lignin chromophores having strong susceptibility to oxidation upon UV irradiation. Lignin is an UV absorber molecule and energy transferred between 200 nm – 400 nm would initiate this process, with the development of colour inducing intermediate products. Chromophoric functional groups responsible for such behaviour are phenolic hydroxyl groups, double bonds and carbonyl groups that can facilitate the formation and stabilisation of free radicals under UV radiation [39].

In contrast, the humic acid solution exhibited a slow reduction in colour upon UV-irradiation (Fig. 1(c)). The colour reduction was non-linear with UV-irradiation time at both wavelengths tested (Fig. 1(c)). A similar phenomenon was previously reported for humic acid solutions upon γ-irradiation. The non-linear reduction in colour intensity of the humic acid solutions with γ-radiation dose was linked to complex radical formation leading to an oxidative degradation to smaller and more acidic, hydrophilic fragments [40].

The rate of colour development of the wastewater effluent was very similar to that of LSA (Fig. 1(a–b)). This suggests lignin based

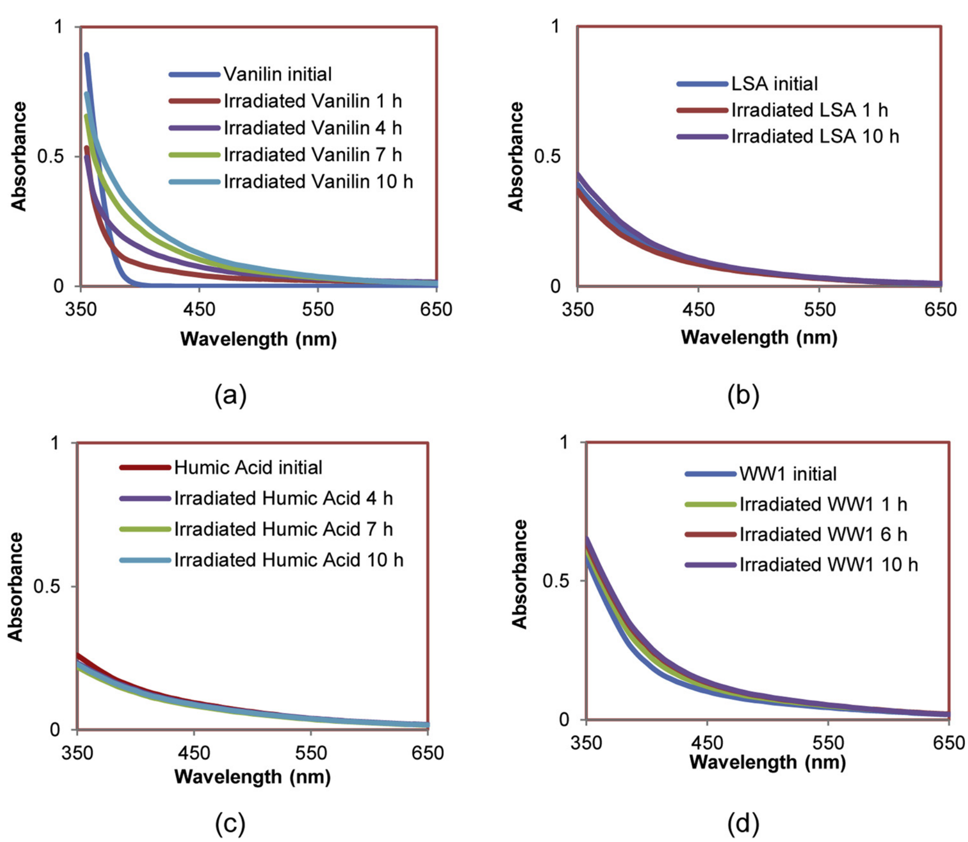

Fig. 2. Wavelength scans of wastewater and model compound solutions irradiated at 302 nm for different periods (0 h, 4 h, 7 h and 10 h): (a) vanillin, (b) lignosulfonic acid (LSA), (c) humic acid and (d) wastewater (WW1).

components play a dominant role in wastewater colour development.

The colour development of process wastewater, LSA and vanillin aqueous solutions upon UV irradiation was more pronounced at 302 nm than at 254 nm. For paper, the literature [31,41] frequently relates chromophores of lignin and derivatives as the main progenitors of photoyellowing. This is attributed to paper functional groups adsorbing the UV portion of sunlight in the region between 300 nm and 400 nm [13,32,41,42]. Thus, the more pronounced colour development of lignin derivatives in aqueous solutions was probably due to the optimal absorption by the chromophores at 302 nm.

3.2. UV spectroscopy

The literature on paper yellowing reveals that the chromophoric groups that intensify upon UV irradiation are typically phenolic OH-groups, quinones, α-carboxyl groups, biphenyls and conjugated double bonds [32,39]. The colour generation of the magnesium bisulphite pulp mill wastewater and some model compounds of this study may well follow a similar mechanism. To confirm the formation of any possible chromophores, the UV spectra of all solutions before and after irradiation were analysed (Fig. 2).

Vanillin solutions prepared were initially colourless. The marked increases in UV absorbance between 350–550 nm upon UV-irradiation indicates the presence of newly formed coloured components. Jethwa et al [36] report that ethanolic solutions of vanillin were converted by the action of sunlight into 6,6′-dihydroxy-5,5′-dimetoxy-1,1′-biphenyl-3,3′-dicarbaldehyde (dehydrodivanillin). The conversion was accompanied by the formation of yellow colour and a slight bitter taste. The UV absorption of the newly formed dehydrodivanillin exhibited a wide shoulder at 337 nm [43].

For humic acid, the UV absorbance between 350–450 nm decreased upon irradiation at all wavelengths measured (Fig. 2(d)). A reduction of colour of humic acid solutions from dark brown to pale yellow upon γ-irradiation was similarly reported by Gorączko et al. [40]. The UV absorbance of humic acid solutions at 270, 400, and 600 nm has been related to the degradation of long wavelength absorbing chromophores into simpler aliphatic compounds [40].

For wastewater and LSA, the slight increases in UV absorption between 350–450 nm are suspected to result from the formation of quinones originating from phenoxyl radicals [32]. All quinone metabolites typically have near identical UV–vis spectra absorbance maxima between 350–500 nm [32,44,45].

3.3. High performance liquid chromatography (HPLC)

Wastewater and model solutions after UV-irradiation were characterised by HPLC. HPLC with a UV-detector can separate components in solution and indicate chemical composition changes occurring upon irradiation. For the wastewater and LSA solutions, complete separation was not achievable due to the complexity (number of similar isomers) of the mixtures [46] (Fig. 3(a–b)). However, the technique proved useful for illustrating changes that occurred in these solutions [46,47].

The HPLC chromatogram of vanillin exhibited the formation of new compounds upon UV irradiation signified by the occurrence of new peaks in the irradiated vanillin chromatogram (Fig. 3(a)). The data shows new products have formed upon irradiation with new peaks appearing at retention times (RT) of 3.7, 4.3 and 5.1 min. The irradiated vanillin solution was further analysed by MS and NMR.

UV-irradiation of the wastewater and the LSA solution did not show significant changes in the overall pattern of the chromatogram, suggesting no major variation in chemical composition (Fig. 3(b–c)). However, there were changes in relative intensity of some peaks, particularly growing peaks at 4.3 and 3.5 min. For LSA, a marked decrease in peak intensity at retention time 2.5 min. appeared. The peak enhancements occurred more markedly for the higher molecular weight components with longer retention times. This suggests condensation of lower molecular weight components, perhaps by dimerization reaction. This observation could also be due to an increase in conjugated double bonds systems which results in better UV detection (greater sensitivity).

The trends in the development of PtCo colour, the HPLC chromatograms and the UV spectra over time, both for the LSA and the wastewater solutions, are very similar (Figs. 2 and 3). This suggests that the components predominating in the process wastewater may have similarities with LSA. The magnesium bisulphite pulping process uses an acidic bisulphite solution as a delignifying medium [48]. Lignin removal from wood commences with cleavage at the α-C atom of the lignin monomer unit followed by the addition of a -SO_3H group to the intermediary carbonium ion. The sulfonation reaction increases the hydrophilicity of lignin, thus increasing its solubility in aqueous liquor [49].

3.4. Mass spectrometry (MS) and Nuclear Magnetic Resonance (NMR) of vanillin

Due to its simple structure, the MS and NMR spectra of vanillin before and after UV irradiation can be readily interpreted. The formation of dimers is evident from the MS spectra (supplementary material). The MS of vanillin solution after 302 nm UV-irradiation shows the appearance of two new peaks at m/z 167 and 301. The peak at m/z 301 noticeably increases in intensity with irradiation time. This peak represents a dimer of vanillin. The structure of this irradiated vanillin product was further analysed by proton NMR spectroscopy (Fig. 4). The initial vanillin exhibits six distinguishable peak clusters easily assigned to the molecular structure (Fig. 4a) [50]. The NMR spectrum of irradiated vanillin shows a similar pattern with an additional peak at 7 ppm (Fig. 4b). The peak at 6.9 ppm is still observed, but at a significantly reduced intensity. This suggests a marked loss of H2 and/or H3 protons, also supporting the formation of a dimer. The vanillin sample was likely a mixture of monomer and dimer because the peaks of the initial sample are also in the irradiated sample. The singlet at 3.6 ppm is split into 3.671 and 3.651 ppm, whereas the singlet initially present at 9.575 is altered to 9.642 together with a very small additional peak.

3.5. FTIR analysis

Differences in the wastewater and LSA solutions before and after irradiation were investigated using difference spectra [Δ(irradiated sample – initial)], as illustrated in Fig. 5). For both samples, reductions in −OH absorption (at 3500 cm^{-1}) and C–O absorptions (alcohols and ethers, e.g. at 1200 cm^{-1}) were found. This is consistent with the formation of quinones as this pathway involves changes in hydroxyl and ether groups by radical attack, together with the formation of carbonyl groups and double bonds. Slight increases in absorption peaks at around 1558 cm^{-1} and 1505 cm^{-1} (for wastewater) and at 1557 cm^{-1} (for LSA) may be attributed to the C=O stretching mode of the protonated semiquinone radicals [51].

The difference spectra for vanillin were less distinct and these samples were more usefully characterised by the NMR, MS and HPLC data already presented.

3.6. Colour generation mechanism

For vanillin, the formation of dimer as a pathway for colour generation is strongly supported by MS and NMR analysis (Fig. 4). The OH radical is typically one of the primary radicals that forms upon UV-irradiation, initiating a series of oxidative transformations [52]. Being electrophilic in nature, the OH radical may attack the electron-rich aromatic rings in vanillin resulting in a phenolic coupling reaction to form divanillin. Divanillin, of molecular weight 302, is formed upon irradiation and increases in concentration with irradiation time (Fig. 6a). The formation of divanillin is observed via the fragment ion at m/z 301 $(M-1)^+$ and from NMR spectra (Fig. 4). A marked decrease of

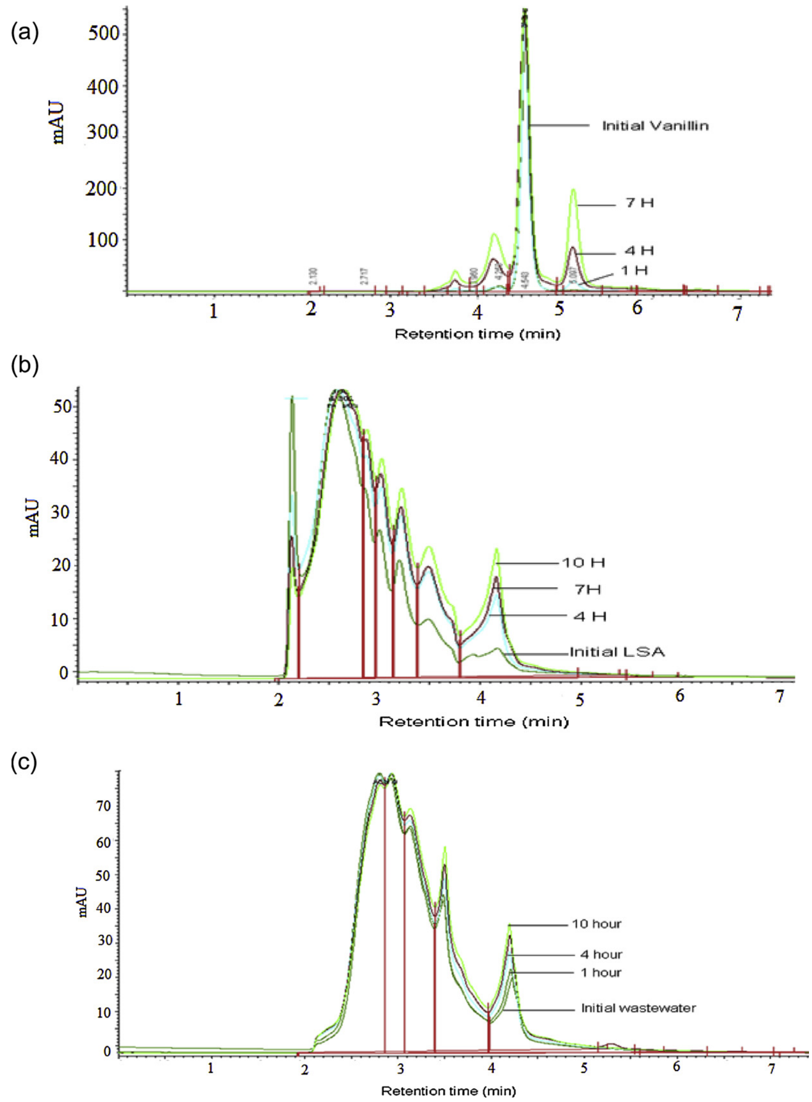

Fig. 3. HPLC chromatogram of sample solutions upon UV irradiation for different periods (1 h, 4 h and 10 h): (a) vanillin, (b) LSA and (c) wastewater.

intensity of the peak at 6.9 ppm indicates that the protons at the H2 and/or H3 position diminish, most likely due to the formation of the biphenyl linkage.

Among the constitutive components of lignin, phenols are the most important [53] and vanillin (4-hydroxy-3-methoxybenzaldehyde) is a typical representative of this group. One of the mechanisms involved in the yellowing of lignocellulosics in aqueous solution includes a phenolic coupling reaction as suggested by the formation of vanillin dimers upon UV-irradiation. A possible pathway of UV-irradiated product of lignocellulosic material, namely the phenacyl pathway [32] has been reported (Fig. 6b). The trends in HPLC chromatograms, UV wavelength scan and FTIR spectra all support the formation of quinone structures in wastewater and LSA solution as a result of UV-irradiation. This is consistent with the commonly accepted pathway of paper yellowing [34].

Carter [13] report that the primary chromophores of lignin typically absorb near UV light (300–400 nm) resulting in free radicals. This is consistent with our findings which report a slower rate of degradation from irradiation at 254 nm relative to 302 nm because of limited free radical formation. These free radicals react with lignin to produce phenoxy and ketyl radicals that may further oxidize to form yellow quinones (Fig. 6). These quinones act as secondary chromophores absorbing light that lead to further colour generation process [13].

The acidic bisulphite pulp mills provide an invaluable industrial model for modern biorefineries. In the last decade, steam explosion pretreatment has become the established pre-treatment for subsequent enzymatic treatment and fermentation of the saccharides into useful products such as ethanol, lactic acid, succinic acid and 1,3 propanediol [54]. As typically applied, without catalyst addition, steam explosion is an auto-catalyzed acidic treatment [49,55]. Effluents from bisulfphite pulp mills are notorious for their colour generation propensity. Typically leaving the pulp mill as clear effluents after the standard primary and secondary treatments, these effluents can become strongly coloured with time.

Here we have demonstrated, by using process water and aqueous solutions of model compounds, that some lignin derivatives do increase in colour intensity upon UV exposure. We have further related the rate of industrial process water yellowing to that of the model lignosulphonate acid (LSA), supporting the hypothesis. This was reinforced by the limited yellowing of humic acid, a phenolic compound of different structure relative to lignin and LSA. Further, the mechanism of yellowing was related to UV induced dimerization of phenolic monomers, using vanillin as model.

This study provides understanding that might mitigate effluent colour development in potential modern biorefineries. Lignin residues are noted in pulp and paper industry for their resistance to secondary water treatment [56–58]. This study have shown that the release of lignin phenolic monomers might be the basis of colour development

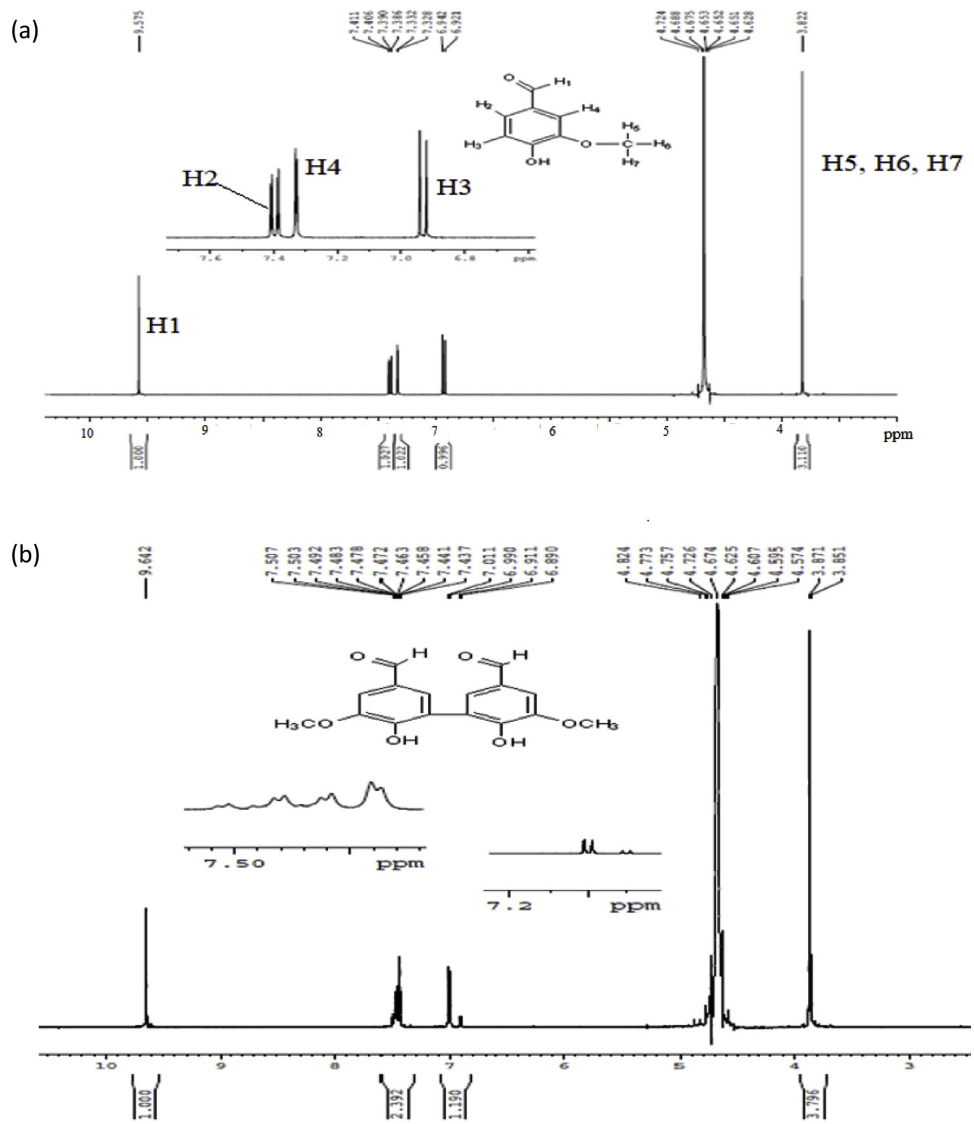

Fig. 4. MS and NMR spectra of vanillin solution: (a) Initial solution, (b) Irradiated 7 h (302 nm).

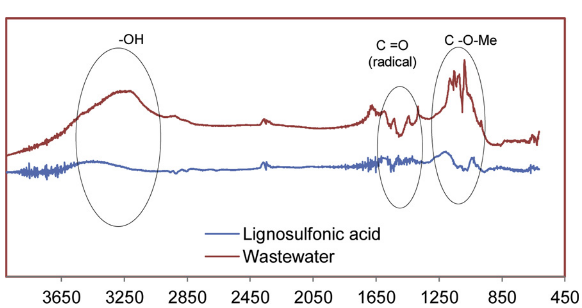

Fig. 5. Difference in FTIR spectra of wastewater and LSA solutions after 7 h of 302 nm UV-irradiation.

due to their dimerization into colour compound upon UV irradiation. A remediation method that could remove or deactivate these reactive moieties could be expected to suppress colour development.

4. Conclusion

This study aimed to gain better understanding of the mechanisms of colour generation of biorefineries process wastewater using model compounds in comparison with the effluent of a bisulphite pulp mill. Process water and model compound solutions were irradiated at 254 nm and 302 nm for various periods of time. It was found that the colour generation is faster upon UV irradiation at 302 nm than that at 254 nm. The colour generation rate follows this trend: vanillin > lignosulfonic acid ˜ wastewater solution. The colour growth of the wastewater effluent was similar to that of the LSA solutions, suggesting lignosulfonates as the precursor for colour generation. Similar to the yellowing of paper from high yield pulps, the effluent from lignocellulosic materials or forest biorefineries are likely to generate colour with time and upon sunlight exposure due to traces of refractory lignin compounds. The main mechanism was related to lignin monomer polymerization. The UV-induced dimerization of vanillin into divanilin was identified by MS and NMR. Aqueous discharges from the biorefinery industry should have minimal levels of phenolic organics so that colour formation induced by UV/sunlight is also minimized.

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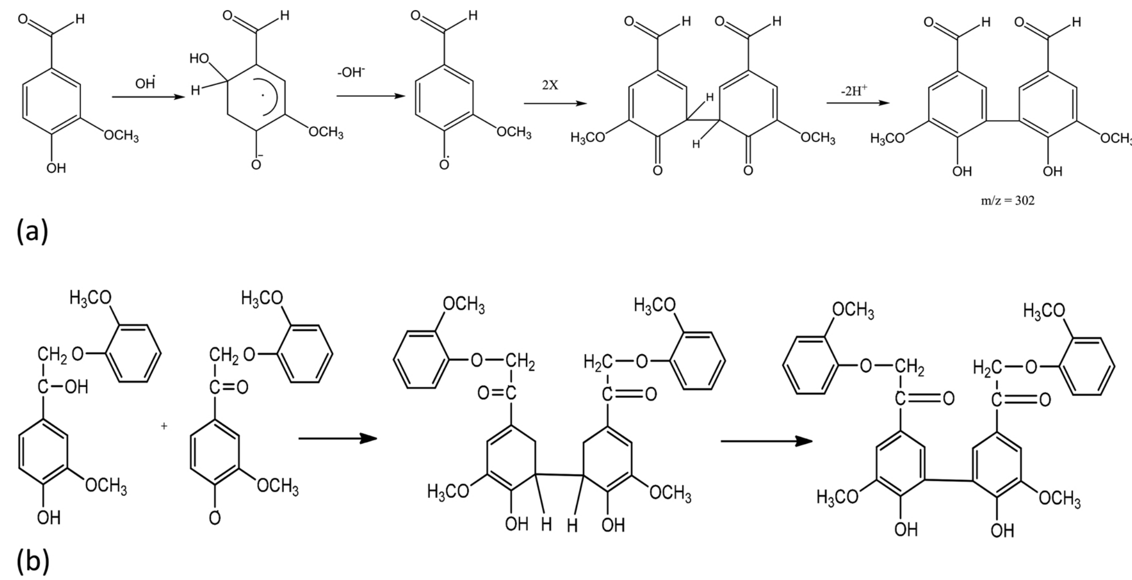

Fig. 6. (a) Proposed mechanism of divanillin formation upon UV-irradiation (formation of divanilin), and (b) the suggested phenacyl pathway for UV-irradiated product formation from lignocellulosic materials: The phenacyl pathway [32].

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jwpe.2019.100781.

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