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# Oxidative depolymerization of lignosulfonates to low-molecular weight aromatics: an interlaboratory study

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In the pursuit of sustainable chemical production, feedstock diversification is essential. Lignosulfonates, a water-soluble aromatic byproduct of the sulfite pulping process, offer a green alternative for producing value-added compounds such as vanillin *via* oxidative depolymerization. However, current depolymerization processes are not comparable due to inconsistencies in feedstocks and a lack of validated analytical methods. In the present study, we developed and validated a novel sample preparation and GC/FID method for quantifying vanillin, vanillic acid, and acetovanillone. Three oxidation processes—continuous alkaline (CA), heterogeneous metal-catalysed (HMC), and electrochemical nickel anode (ENA)—were optimized and compared using the same feedstock. A round-robin test ensured analytical comparability across different labs. The analytical method demonstrated high precision (<5% intra-lab, <10% inter-day, and <25% inter-lab RSD) for all compounds. The HMC oxidation process yielded the highest total monomer concentration (4.3 g L<sup>-1</sup>) and monomer yield (8.7 wt%), while CA oxidation achieved the highest volumetric productivity (up to 840 g (L × h)<sup>-1</sup>). Future work should explore hybrid approaches leveraging the strengths of these oxidative lignin depolymerisation processes.

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## Sustainability spotlight

Lignin is a major renewable component of biomass, yet its potential as a sustainable chemical feedstock remains largely untapped. By enabling systematic evaluation of different depolymerisation strategies, our work supports the development of more efficient and environmentally conscious valorisation pathways. These advances promote responsible production, foster innovation in industrial processes, and help reduce the environmental impact of chemical manufacturing. Ultimately, this research contributes to a circular bioeconomy, where renewable resources are utilized more effectively, industrial processes are optimized for sustainability, and carbon footprints are minimized.

## Introduction

For over two centuries, nearly all human activities have depended on reliable access to fossil-based fuels and chemicals. Although many countries are currently investing in energy diversification, the same cannot be said for chemical feedstocks, 90% of which are produced from oil and gas.<sup>1</sup> This almost exclusive dependence is a concern with regard to sustainability and therefore one of the key drivers in the use of renewable, bio-based feedstocks.<sup>2</sup> One such feedstock is lignin, a phenolic biopolymer that is abundant in plant biomass.

Lignins consist primarily of three phenolic monomers with an allylic alcohol sidechain, characterized by their phenolic part being either a 4-hydroxyphenyl, guaiacyl, or syringyl.<sup>3–5</sup> The monomers are bound together by a variety of ether and carbon-carbon bonds.<sup>3,6</sup> The relative abundance of the different monomers and linkages varies between different plant

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species.<sup>7,8</sup> In pulp and paper mills, lignin represents a side-stream product most commonly incinerated to produce process energy in the form of steam and recover process chemicals.<sup>9–11</sup> Only 2% of the lignin produced is extracted and sold as technical lignin for value-added applications.<sup>12</sup>

Lignosulfonates are water-soluble technical lignins produced in the sulfite process that are used as dispersants, binders, and composite materials.<sup>10</sup> Due to their abundance in guaiacyl units, softwood lignosulfonates are also used as feedstock in the production of vanillin, which is commonly produced from petrochemical feedstocks.<sup>13,14</sup> Vanillin has a wide range of uses, such as in flavourings, cosmetics, and as a starting material for production of pharmaceuticals.<sup>15,16</sup>

An efficient and environmentally sustainable depolymerization technology is required for the conversion of lignin into value-added products such as aromatic intermediates. Numerous approaches for lignin depolymerization have been explored *via* reductive, oxidative (Fig. 1), acid-catalysed, base-catalysed, and thermal methods.<sup>17–20</sup> Alkaline aerobic oxidation enables selective production of the aromatic aldehydes vanillin and syringe aldehyde from lignin, and is carried out commercially to produce vanillin from lignosulfonates.<sup>21–23</sup> Common side-products include vanillic acid and acetovanillone.

Metal-based catalysts, both homogeneous and heterogeneous, have been used to improve monomer yield and selectivity.<sup>23,24</sup> Homogeneous catalysis with cobalt or copper salts has shown high vanillin yields in the alkaline aerobic oxidation of lignosulfonates.<sup>13</sup> Recovery and recycling of homogeneous catalysts is complex, and heterogeneous catalysts have therefore been evaluated for lignin oxidation to improve cost-effectiveness.<sup>25,26</sup> The integrity of many heterogeneous catalysts is compromised under alkaline conditions, and only a few examples of alkaline aerobic oxidation of lignin with heterogeneous catalysts have been reported.<sup>27,28</sup>

Electrochemical oxidative depolymerization of lignin offers a means of minimizing reagent waste while still ensuring high vanillin yields.<sup>29</sup> As far back as 1988, a patent (US4786382A) was granted for nickel anode oxidation of lignin. Since then, this method has been experimentally evaluated in different setups using Kraft lignin,<sup>30–32</sup> organosolv lignin,<sup>16,33</sup> and lignosulfonates<sup>15,34</sup> as raw material.

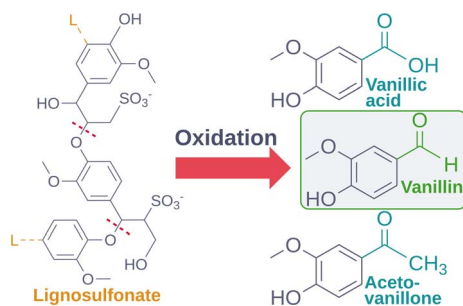


Fig. 1 Oxidative depolymerization of a lignosulfonate substructure (linked to a larger lignin polymer, L) into three common products. Cleavable bonds are shown as red dashed lines.

The yields of low molecular weight (MW) compounds from lignin depolymerization processes are controlled by the abundance and accessibility of  $\beta$ -O-4 ether linkages.<sup>35</sup> Therefore, when comparing different processes, feedstock choice is crucial. To mitigate feedstock selection bias, yields are often normalized by a theoretical maximum yield, *e.g.*, the yield from nitrobenzene oxidation.<sup>36</sup> However, this has led to contradictory yield definitions in the literature. Additionally, many different analysis methods are in use, and most are poorly characterized, which can introduce analytical biases in the estimates.<sup>37</sup> Previous inter-laboratory studies have been limited to determination of total lignin<sup>38,39</sup> or molar mass,<sup>40</sup> meaning such biases are unknown for low MW compounds. These challenges hinder the evaluation and implementation of state-of-the-art approaches to lignin depolymerisation, impeding the transition toward a sustainable bioeconomy.

For this comparative study, an analytical method for rapid and robust quantification of vanillin, vanillic acid, and acetovanillone was developed and thoroughly validated, which included a round-robin test. This method enabled a unique and accurate comparison between three distinct oxidative depolymerization techniques: continuous alkaline (CA), heterogeneous metal-catalysed (HMC), and electrochemical nickel anode (ENA), performed in three independent research laboratories using the same lignosulfonate feedstock.

## Experimental

### Continuous alkaline (CA) oxidation

A modified Parr 5400 series continuous-flow tubular reactor system, including a 40 mL tubular reactor and a 130 bar back-pressure regulator was used. The reaction mixture, consisting of lignosulfonate and 4 M NaOH, was fed into the reactor. Additionally, specified quantities of a 10 wt%  $\text{H}_2\text{O}_2$  solution were added to the reaction mixture before entering the reactor. The reactor was heated externally using an electric furnace, and the flow was adjusted to maintain a residence time of 12 seconds. The specified temperature corresponds to the exit temperature of the reaction mixture. Temperature (200–280 °C), lignosulfonate (35–118  $\text{g L}^{-1}$ ), and  $\text{H}_2\text{O}_2$  (0–10  $\text{g L}^{-1}$ ) concentrations were optimized for the highest yield of phenolic monomers (vanillin, acetovanillone, vanillic acid and the sum of these, *i.e.* total monomer yield) using a factorial design (Table S1). For each experiment, a minimum of 100 reactor volumes were run before a sample was collected. The reaction mixture was cooled to below 100 °C using a heat exchanger before releasing pressure and samples were collected at atmospheric pressure and 50–70 °C. The process was repeated three times at the estimated optimal conditions.

### Heterogeneous metal-catalysed (HMC) oxidation

A Cu–Co/ZrO<sub>2</sub> catalyst (Cu–Co molar ratio of 1 : 1, 15 wt% metal loading) was prepared by impregnating ZrO<sub>2</sub> twice with a copper (ii)acetate and cobalt (ii)chloride solution. After each impregnation, the catalyst was dried at 100 °C for 4 h and calcined at 450 °C for 8 h in a Thermolyne 6000 muffle furnace.



Depolymerization was performed in a 50 mL autoclave with a heating plate and a thermocouple. A 20 mL lignosulfonate solution ( $50 \text{ g L}^{-1}$ ) in 2 M NaOH and a metal co-catalyst were added, and the autoclave was purged and charged with  $\text{O}_2$ . The reactor operated at 500 rpm and a reaction time of 10 min after reaching the specified temperature. Temperature ( $160\text{--}200 \text{ }^\circ\text{C}$ ),  $\text{O}_2$  pressure (3–7 bar), and catalyst amount (0.25–0.75 g) were optimized for highest phenolic monomer yield using a Box–Behnken design, constructed and evaluated in the Stat-Ease® 360 software (Stat-Ease, Inc., Minneapolis, MN, USA) (Table S2).<sup>41</sup> The reaction was finally performed in triplicate at the optimal operating conditions.

Characterization of the catalyst used at optimal operating conditions was performed using  $\text{N}_2$  physisorption, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), scanning electron microscopy energy dispersive X-ray spectroscopy (SEM-EDX), and inductively coupled plasma optical emission spectrometry (ICP-OES).

### Electrochemical nickel anode (ENA) oxidation

An electrochemical reactor was set up using a 50 mL stainless steel autoclave lined with Teflon. The autoclave includes a flange with a manometer, a pressure release valve, and an over-pressure valve rated at 8 bar. Within the autoclave there were  $2 \times 6 \text{ cm}$  nickel electrodes with an active area of  $6 \text{ cm}^2$  for the electrolysis. Electrolysis was conducted at room temperature with stirring at 300 rpm. Lignosulfonate was dissolved in aqueous NaOH (3 M, 50 mL). The resulting solution was transferred to the autoclave, which was then sealed. The electrodes were connected to an electrical source, and galvanostatic electrolysis was initiated, followed by a subsequent thermal post-treatment. First, a fractional factorial ( $2^{5-2}$ ; one-quarter fractional factorial design) design was employed to optimize applied charge (2–4 C  $\text{mg}^{-1}$ ), current (6–30 mA), lignosulfonate concentration ( $5\text{--}20 \text{ g L}^{-1}$ ), post-treatment temperature ( $130\text{--}170 \text{ }^\circ\text{C}$ ), and post-treatment heating time (12–24 h) on the yield of phenolic monomers (Table S3). Then, a full-factorial design was conducted within the same ranges, but with the lignosulfonate concentration kept constant at  $5 \text{ g L}^{-1}$  and with a post-treatment heating time of 18 h (Table S4). The reaction mixtures were cooled to room temperature after depolymerisation. The reaction was finally performed in triplicate at the optimal operating conditions. ICP-OES, using external calibration and mean estimates from measurements at five wavelengths in triplicate, was employed to estimate Ni-ion leakage from the anode.

### Development of a monomer quantification method

3-Ethoxy-4-hydroxybenzoic acid (ethyl vanillic acid) was synthesized by Borregaard AS. All other chemicals were obtained from Sigma-Aldrich at reagent grade or higher. A representative softwood lignosulfonate sample (prepared by CA oxidation at Borregaard AS) was used for method development and initial validation. A 3 mL sample of the crude reaction mixture was spiked with internal standards, acidified to pH 1–2 using 3 mL of aqueous (6 M) HCl or  $\text{H}_2\text{SO}_4$  and vortexed with

a glass bead. Then, 3 mL ethyl acetate were added, and the sample was vortexed again. A stable solid agglomerate formed spontaneously at the ethyl acetate/water interface, allowing for the monomer-containing organic phase to be collected without centrifugation. The aqueous and solid phases were reextracted twice with ethyl acetate, pooled and immediately analysed, or stored at  $4 \text{ }^\circ\text{C}$  to prevent re-polymerization. Internal surrogate standards, ethyl vanillin for vanillin and ethyl vanillic acid for vanillic acid, dissolved in ethyl acetate were added to all samples prior to analysis by gas chromatography with flame ionization detection (GC-FID).

Eighteen phenolic standards, representing plausible monomeric products, were dissolved in ethyl acetate at equimolar amounts and used to optimize the GC-FID analysis with respect to detectability and resolution. The final method employed a DB-5 column ( $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ }\mu\text{m}$ ), a  $1 \text{ }\mu\text{L}$  split (10 : 1 or higher) injection at  $290 \text{ }^\circ\text{C}$ , a  $\text{N}_2$  flow rate of  $1 \text{ mL min}^{-1}$  with a column oven temperature increasing from  $150 \text{ }^\circ\text{C}$  to  $190 \text{ }^\circ\text{C}$  by  $10 \text{ }^\circ\text{C min}^{-1}$ , and  $190 \text{ }^\circ\text{C}$  to  $310 \text{ }^\circ\text{C}$  by  $40 \text{ }^\circ\text{C min}^{-1}$ , where it was held for 5 min. The FID was maintained at  $320 \text{ }^\circ\text{C}$  with air,  $\text{H}_2$ , and  $\text{N}_2$  supplied at 400, 40, and  $40 \text{ mL min}^{-1}$ , respectively. The monomer yields were calculated as the mass ratio of monomer to feedstock.

### Validation of the monomer quantification method

Lower limit of quantification (LLOQ) was determined based on relative standard deviation (RSD) at each calibration level using a threshold of 5% RSD. The linear range was determined by removing calibration levels until reaching a percentage residual accuracy (% RA) above 95%.<sup>42</sup> The method was validated in three independent labs using the same CA oxidation batch, shipped at below  $0 \text{ }^\circ\text{C}$  in dark containers to each participant. An extensive analytical protocol and a standard calculation spreadsheet, together with personal instrument training, were supplied to all partners. Repeatability was determined from triplicate analysis conducted on three consecutive days, providing a robust estimate of intraday precision. Interday precision was estimated using all 27 possible permutations between the days and reported as the range and mean for resulting RSDs. Inter-lab reproducibility was estimated from an anonymised round-robin test and estimated as the relative bias *versus* the grand mean, due to the lack of well-characterized reference materials. The precision targets were 5% and 20% RSD for within and between lab, respectively. Biases in the analyses were estimated using analysis of variance (ANOVA).

## Results and discussion

### Screening and optimization of reaction conditions

For CA oxidation, vanillin and the total monomer yield were significantly influenced by temperature and lignosulfonate concentration, with high temperatures positively correlating with total monomer yield, while lignosulfonate concentration exhibited a negative correlation. The maximum monomer yield was obtained at a temperature ( $280 \text{ }^\circ\text{C}$ ) and  $\text{H}_2\text{O}_2$  concentration



(10 g L<sup>-1</sup>) in the higher range and liginosulfonate (35 g L<sup>-1</sup>) in the lower range of investigated factors (Table S5).

For HMC oxidation, the optimal operating conditions for maximum monomer yield was found in the upper range of temperature (200 °C), O<sub>2</sub> pressure (7 bar) and amount of catalyst (0.65 g) (Table S6). All variables significantly impacted vanillin yield, with temperature having the greatest effect (ANOVA,  $p < 0.0001$ ), compared to pressure ( $p = 0.012$ ) and catalyst amount ( $p = 0.011$ ). A control experiment conducted in absence of catalyst resulted in a vanillin and total monomer yield of 5.3% and 6.6%, respectively. Hence, a 32% increase in both vanillin and total monomer yield was obtained in presence of catalyst. The spent catalyst had a slightly higher specific surface area than the fresh catalyst, presumably due to carbon deposits; no difference was observed in pore volume or size (Table S7). The catalyst showed good thermal stability, with the spent catalyst exhibiting a 0.5 wt% weight loss after 260 °C, probably due to release of organic compounds (Fig. S1). However, leaching of Cu (32 500 and 22 200 mg kg<sup>-1</sup> in fresh and spent catalyst, respectively) and Co (49 900 and 37 500 mg kg<sup>-1</sup>, respectively) was observed (Fig. S2 and Table S8). This highlights the need for further development of both the catalyst and reactor configuration before industrial application, in order to limit ecological consequences and avoid the need for economically unfeasible purification units.

The optimum conditions for ENA oxidation were found at an intermediate post-treatment heating time (18 h), showing almost no influence on the yield of monomers, with the concentration of liginosulfonate (5 g L<sup>-1</sup>) and applied charge (2 C mg<sup>-1</sup> substrate) in the lower range and current density (30 mA cm<sup>-2</sup>) and post-treatment heating temperature (170 °C) in the upper range of the investigated factors (Tables S9 and 10). The optimum liginosulfonate concentration is low, which also results in a low productivity. To render this process more viable, the concentration could be increased albeit with a slight loss of relative yield of monomers. However, achieving the same level of productivity as the CA oxidation is unrealistic, given the much longer reaction times of the ENA oxidation. A very small leakage of Ni ions was observed from the electrodes after electrolysis (47.4 ppb vs. 38.9 ppb in a blank, which increased after the thermal post-treatment (137.6 ppb) (Table S11). Hence, an advantage of ENA oxidation is its resource efficiency, since the electrodes show little degradation and the sodium hydroxide could be reused by efficient downstream processing, e.g., using ion exchange resins. An exploration of ENA oxidation on a larger semi-continuous scale could be beneficial.

### Development of a lignin quantification method

The total sample preparation time was less than 15 minutes, which is considerably faster than previous methods which have applied tedious vacuum filtration and centrifugation steps.<sup>43</sup> The new method instead benefits from the tendency of liginosulfonate to agglomerate at low pH in the presence of an organic solvent (illustrated in Fig. 2a), allowing the monomer-rich organic phase to be effortlessly recovered. The agglomeration of liginosulfonate is a phenomenon that is well described in the



Fig. 2 Development of a lignin quantification method. (a) Illustration of the spontaneous formation of a solid aggregate at the phase-boundary during extraction, which allowed for a fast, yet quantitative extraction. (b) Eighteen plausible monomeric lignin products were separated in 6 minutes. The analytes of interest in this study are highlighted, demonstrating a sufficiently high resolution to avoid peak interference even at higher concentrations. Remaining details are found in Table S12.

literature,<sup>44</sup> for instance in the field of flocculation research,<sup>45</sup> but not in the context of analytical extractions. The extraction recoveries for ethyl vanillin and ethyl vanillic acid from spiked samples were used to estimate the recoveries for the analytes. The extraction recoveries were quantitative, even after just one extraction (Fig. S3). Despite this, three consecutive extractions were chosen to ensure sufficient robustness of the method, while maintaining a reasonable workload. Performing a single extraction would reduce the sample preparation time to 5 minutes. The final GC-FID method was able to resolve most of the 18 plausible monomeric products in six minutes (Fig. 2b and Table S12). Syringol alcohol and caffeic acid were not resolved, but their concentrations were expected to be negligible in softwood liginosulfonates.

### Validation of the lignin quantification method

The LLOQ was around 30 µg mL<sup>-1</sup>, with a working range spanning at least three orders of magnitude for all three analytes. Five calibration levels were deemed appropriate for the further work with a linear range spanning two orders of magnitude. All within-lab precision estimates met the <5% RSD target, except for acetovanillone, which was near the LLOQ (Tables 1 and S13). The negligible difference between intra- and

Table 1 Mean analytical reproducibilities for each analyte, determined using a representative sample of CA oxidation liquor from softwood liginosulfonate. The reproducibilities were estimated as relative standard deviations and included contributions from the extraction

| Estimate               | Vanillin | Vanillic acid | Acetovanillone |
|------------------------|----------|---------------|----------------|
| Intra-day ( $n = 3$ )  | 2.3%     | 2.0%          | 1.9%           |
| Inter-day ( $n = 27$ ) | 1.9%     | 2.5%          | 6.2%           |
| Inter-lab ( $n = 3$ )  | 5.3%     | 22.5%         | 12.8%          |



**Table 2** Average monomer yields in weight percent performed at optimized conditions for each depolymerization method with the relative standard deviation of % yield provided within parentheses

| Method       | Vanillin (RSD) | Vanillic acid (RSD) | Acetovanillone (RSD) |
|--------------|----------------|---------------------|----------------------|
| CA           | 6.6% (3.1%)    | 0.7% (16.3%)        | 0.5% (8.3%)          |
| HMC          | 7.0% (2.8%)    | 0.9% (3.1%)         | 0.8% (2.7%)          |
| ENA          | 6.3% (2.9%)    | 0.7% (3.3%)         | 0.9% (13.9%)         |
| Nitrobenzene | 10.6% (4.3%)   | —                   | —                    |

**Table 3** Total monomer concentrations, reaction times and volumetric productivity rates for each depolymerization method

| Method | Total monomer concentration (g L <sup>-1</sup> ) | Reaction time (h) | Volumetric productivity (g (L <sup>-1</sup> × h <sup>-1</sup> )) |
|--------|--|-------------------|--|
| CA     | 2.8  | 0.003             | 840  |
| HMC    | 4.3  | 0.17              | 26   |
| ENA    | 0.4  | 21                | 0.02   |

inter-day estimates for vanillin and vanillic acid concentrations indicated high internal robustness. No bias was observed with respect to vanillin quantification in the three independent laboratories (ANOVA,  $p > 0.05$ ) (Tables 1, S14 and Fig. S4). However, biases were observed in the reported concentrations for acetovanillone and vanillic acid (ANOVA,  $p < 0.01$ ). This most likely related to their low concentrations relative to vanillin, which was favoured when diluting the samples for analysis. Both vanillin and acetovanillone showed an inter-laboratory reproducibility well below the common acceptance criteria of an RSD <20%.<sup>46,47</sup> As such, this round-robin test was able to demonstrate that monomeric yields determined in different laboratories can be reliably compared, if the same lignin feedstock and analytical method is used.

## Comparison of lignin depolymerisation methods

Each of the oxidation protocols were repeated three times on the same feedstock at the optimized conditions and monomer yields estimated using the validated GC-FID method (Table 2). Yields of all three quantified monomers differed between methods (ANOVA,  $p < 0.05$ ). For vanillin, HMC was found to perform better than ENA (Tukey's post hoc test,  $p = 0.011$ ), while CA produced less acetovanillone than both HMC ( $p = 0.0074$ ) and ENA ( $p = 0.0017$ ). The yield of vanillic acid was higher for HMC than for CA ( $p = 0.028$ ) and ENA ( $p = 0.028$ ).

Furthermore, when assessing total monomer concentrations, HMC outperformed the other methods, achieving 4.3 g L<sup>-1</sup> total monomer (Table 3). This finding has significant implications for downstream processing economics, as higher product titers equate to smaller process volumes. However, CA emerged as the most efficient reaction method in terms of reaction time. Despite achieving only 65% of the total monomer concentration achieved by HMC, CA exhibited a volumetric productivity rate 32 times higher than that of HMC. Hence, the reactor volume required to produce 1000 tons of vanillin per year would be only 0.14 m<sup>3</sup> for CA, reflecting its exceptionally

high volumetric productivity. In contrast, the HMC method requires 4.4 m<sup>3</sup>, representing a moderate balance between yield and scalability. The ENA method, however, would require 5708 m<sup>3</sup>, which suggests that it is currently not feasible for industrial-scale production without substantial process improvements. The substantial differences in volumetric yield between the processes render detailed techno-economic or life cycle assessments irrelevant while underscoring the advantages of CA in potential scale-up scenarios.

## Conclusions

This comparative study was enabled by the development and thorough validation of a method for lignin monomer quantification, providing a unique capability to compare processes performed across different laboratories. The comparative analysis of monomer yields revealed that HMC oxidation outperformed CA and ENA oxidation in terms of both total monomer yield and the yield of specific monomers, particularly vanillin. Despite providing lower total monomer yields, CA oxidation exhibited remarkably higher volumetric productivity, impacting both operating and capital expenses in potential scale-up scenarios. For future work, a hybrid approach could be explored, combining the strengths of HMC with the strengths of the other two oxidation processes. For instance, a sequential system combining HMC and CA could improve selectivity, yield, and productivity. Challenges would include catalyst leaching, thermal transitions, and process compatibility.

## Author contributions

M. N.: conceptualization, methodology, validation, formal analysis, investigation, resources, writing – original draft, visualization; S. B.: conceptualization, methodology, validation, formal analysis, investigation, writing – original draft, visualization; J. K.: methodology, validation, investigation, writing – original draft; F. M.: conceptualization, methodology, validation, formal analysis, investigation, writing – original draft; K. P.



J. G.: methodology, formal analysis, writing – review & editing; M. S.: writing – review & editing, supervision; C. P. H.: writing – review & editing, supervision, funding acquisition; C. T.: writing – review & editing, supervision, funding acquisition; O. Y. A.: conceptualization, methodology, software, validation, formal analysis, investigation, resources, writing – review & editing, visualization, supervision; S. R. W.: writing – review & editing, supervision, funding acquisition; P. S.: conceptualization, writing – review & editing, supervision; O. B.: conceptualization, writing – review & editing.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting the conclusions of the article are included within the article and the SI. See DOI: <https://doi.org/10.1039/d5su00698h>.

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