
JOURNAL OF APPLIED CHEMISTRY RESEARCH

(JACR)

A Peer-Reviewed & Refereed International Journal

Volume 01 | Issue 01 | January – June 2026

Inaugural Issue

Journals Published by Adeon Global

www.adeonglobal.com | editor@adeonglobal.com

ABOUT THE JOURNAL

Journal Description

The Journal of Applied Chemistry Research (JACR) is an international, peer-reviewed scholarly journal dedicated to advancing research and innovation across the diverse field of applied chemistry. The journal provides a platform for researchers, scientists, academicians, industry professionals and research scholars to disseminate original research findings and practical developments that contribute to scientific advancement and real-world applications. It is published by Adeon Global, and the present volume is its inaugural issue.

The journal focuses on the application of chemical principles, processes, materials and technologies in areas such as pharmaceuticals, environmental science, materials science, industrial processes, energy, agriculture, nanotechnology, biotechnology and sustainable development. It encourages interdisciplinary research that bridges fundamental chemical knowledge with practical application, and it aims to promote scientific collaboration and the exchange of innovative ideas among researchers from different countries and academic disciplines.

Aim & Scope

The Journal of Applied Chemistry Research aims to promote high-quality scientific research and innovation in applied chemistry by providing an international platform for the publication and dissemination of significant research findings. The journal seeks to encourage the development of innovative chemical technologies, sustainable processes, advanced materials and practical solutions to contemporary industrial, environmental, pharmaceutical, agricultural and technological challenges.

The journal welcomes original research articles, review articles, short communications, technical notes and other scholarly contributions that demonstrate scientific relevance, methodological rigour, originality and potential practical impact. Original and innovative research is invited in, but not limited to, the following areas:

- Applied Chemistry
 - Analytical Chemistry
 - Organic Chemistry
 - Inorganic Chemistry
 - Physical Chemistry
 - Industrial Chemistry
 - Environmental Chemistry
 - Green and Sustainable Chemistry
 - Materials Chemistry
 - Polymer Chemistry
 - Pharmaceutical and Medicinal Chemistry
 - Nanochemistry and Nanomaterials
 - Chemical Process Development
 - Energy and Fuel Chemistry
 - Renewable Energy Materials
 - Water and Wastewater Treatment
 - Environmental Pollution and Remediation
 - Food Chemistry
 - Agricultural and Agrochemical Research
 - Biochemistry and Chemical Biology
 - Biotechnology and Applied Chemical Sciences
 - Surface and Colloid Chemistry
 - Corrosion Science and Protection
 - Chemical Sensors and Instrumentation
-

-
- Computational and Theoretical Chemistry
 - Electrochemistry
 - Catalysis and Chemical Reaction Engineering
 - Advanced Functional Materials
 - Sustainable Industrial Processes
 - Circular Economy and Chemical Waste Management

Publication Frequency and Access Policy

The Journal of Applied Chemistry Research is published half-yearly in two issues per volume, covering the periods January to June and July to December. The journal operates an open-access model: accepted articles are made freely available on the publisher's website without subscription or embargo, and authors retain copyright in their work while granting the journal the right of first publication.

Peer Review Policy

All submissions are screened by the editorial office for scope, completeness and originality, and manuscripts that pass screening are sent for double-blind peer review. Each manuscript is assessed by a minimum of two independent reviewers drawn from the editorial board or from the wider reviewer pool. Reviewers are asked to comment on originality, methodological soundness, adequacy of the supporting data, clarity of presentation and appropriateness of the conclusions. The indicative turnaround from submission to first decision is four to six weeks. Final acceptance rests with the Chief Editor.

Indexing and Abstracting

The Journal of Applied Chemistry Research is a new title and the present volume is its inaugural issue. Application for an International Standard Serial Number is in progress, and the journal has not yet been assigned a Digital Object Identifier prefix; articles in this issue therefore carry no DOI. Applications to indexing and abstracting services will be made once the minimum publication history required by those services has been established. Current registration status is published on the journal's page at www.adeonglobal.com.

EDITORIAL BOARD

No.	Name	Position / Affiliation	Country
1	Prof. Dr. Ahmad Fauzi Ismail	Chief Editor — Professor of Chemical Engineering, International Research Centre for Advanced Materials, Universiti Teknologi Malaysia, Johor Bahru	Malaysia
2	Prof. Dr. Siti Aisyah Ahmad	Professor, Department of Chemistry, Universitas Indonesia, Depok	Indonesia
3	Prof. Dr. Muhammad Iqbal	Professor, Department of Chemical Engineering, Institut Teknologi Bandung, Bandung	Indonesia
4	Dr. Nurul Hidayati	Associate Professor, Department of Chemistry, Universitas Gadjah Mada, Yogyakarta	Indonesia
5	Dr. Rina Kusumawati	Associate Professor, Faculty of Mathematics and Natural Sciences, Universitas Airlangga, Surabaya	Indonesia
6	Dr. Budi Santoso	Associate Professor, Department of Chemical Engineering, Universitas Diponegoro, Semarang	Indonesia
7	Dr. Dewi Anggraini	Senior Lecturer, Department of Chemistry, Universitas Hasanuddin, Makassar	Indonesia
8	Dr. Agus Prasetyo	Associate Professor, Department of Chemical Engineering, Institut Teknologi Sepuluh Nopember, Surabaya	Indonesia
9	Prof. Dr. Noraini Mohamed	Professor, Faculty of Science, Universiti Malaya, Kuala Lumpur	Malaysia
10	Prof. Dr. Mohd Azlan Hussain	Professor, School of Chemical Sciences, Universiti Sains Malaysia, Penang	Malaysia
11	Dr. Nurul Izzati Rahman	Associate Professor, Faculty of Applied Sciences, Universiti Teknologi MARA, Shah Alam	Malaysia
12	Dr. Lim Wei Jian	Associate Professor, Department of Chemistry, Universiti Putra Malaysia, Serdang	Malaysia
13	Dr. Farah Nadia Abdul Karim	Senior Lecturer, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, Bangi	Malaysia
14	Dr. Muhammad Hakim Roslan	Senior Lecturer, Faculty of Chemical and Process Engineering Technology, Universiti Malaysia Pahang Al-Sultan Abdullah, Pahang	Malaysia

CONTENTS

Sr. No.	Title of the Article	Author(s)	Page No.
1	Green Synthesis and Characterisation of Plant-Extract-Mediated Zinc Oxide Nanoparticles for Environmental Remediation: A Model-Based Framework Linking Structural Descriptors to Photocatalytic Performance	A. Sharma, R. Verma, P. Nair, K. Mehta	1
2	Development of Biodegradable Polymer-Based Composite Materials for Sustainable Packaging Applications: A Micromechanical and Barrier Modelling Assessment of Cellulose-Reinforced Polylactide Films	V. Kulkarni, S. Patil, A. Deshmukh, R. Joshi	11
3	Adsorptive Removal of Heavy Metals from Industrial Wastewater Using Modified Agricultural Waste-Derived Biochar: An Isotherm, Kinetic and Thermodynamic Modelling Study	N. Gupta, A. Singh, S. Mishra, R. Yadav	21
4	Electrochemical Performance of Nitrogen-Doped Hierarchical Porous Carbon Nanomaterials for High-Efficiency Supercapacitor Applications: A Descriptor-Based Performance Model	A. Kumar, N. Raj, K. Reddy, M. Saini	31
5	Development and Validation of a Green Analytical Method for the Simultaneous Determination of Pharmaceutical Residues in Water Samples: A Modelling and Greenness Assessment Study	P. Menon, A. Rao, H. Jain, M. Krishnan	41

RESEARCH ARTICLE

Green Synthesis and Characterisation of Plant-Extract-Mediated Zinc Oxide Nanoparticles for Environmental Remediation: A Model-Based Framework Linking Structural Descriptors to Photocatalytic Performance

Dr. Ananya Sharma, Rahul Verma, Priya Nair, Kunal Mehta

Department of Chemistry, Indian Institute of Technology, Roorkee, Uttarakhand, India

ABSTRACT

Plant-extract-mediated synthesis of metal oxide nanoparticles has become one of the most widely reported routes to photocatalysts for wastewater remediation, yet the literature remains difficult to compare because structural descriptors, optical descriptors and kinetic constants are reported under incompatible conventions and are rarely propagated into a single quantitative statement of performance. This article addresses that gap by constructing an explicit, fully specified evaluation framework for phytochemically synthesised zinc oxide, in which every reported number is computed from a declared generating model rather than measured in the laboratory. A wurtzite diffraction dataset was generated for seven indexed reflections from a stated crystallite size of 22 nm and a lattice microstrain of 1.20×10^{-3} , and the resulting line widths were analysed by the Scherrer and Williamson–Hall methods. Scherrer analysis returned a mean crystallite size of 16.9 ± 0.9 nm, whereas Williamson–Hall regression recovered 20.9 nm together with a microstrain of 9.95×10^{-4} at a coefficient of determination of 0.9482, quantifying the systematic underestimate that follows when strain broadening is neglected. Tauc extrapolation of a modelled direct-allowed absorption edge returned a band gap of 3.17 eV against a generating value of 3.18 eV. Photocatalytic decolourisation was modelled by Langmuir–Hinshelwood kinetics; linearisation of initial rates recovered a rate constant of $0.441 \text{ mg L}^{-1} \text{ min}^{-1}$ and an adsorption constant of 0.0350 L mg^{-1} with a coefficient of determination of 0.9987, and apparent first-order constants fell from 0.0116 to 0.0055 min^{-1} as the initial dye concentration rose from 10 to 50 mg L^{-1} . The framework is offered as a reporting and screening template, not as a substitute for experimental validation.

Keywords: *green synthesis; zinc oxide nanoparticles; plant extract; photocatalysis; Langmuir–Hinshelwood kinetics; wastewater treatment; Williamson–Hall analysis*

1. INTRODUCTION

Industrial effluents from textile dyeing, pulp bleaching and pharmaceutical manufacture carry synthetic organic dyes whose aromatic backbones resist conventional biological treatment. Once discharged, these compounds attenuate light penetration in receiving waters, disturb photosynthetic activity and persist long enough to accumulate in sediments. Heterogeneous photocatalysis over wide-band-gap semiconductors, a field opened by the demonstration of photo-assisted water splitting at a semiconductor electrode [7], offers a route to mineralisation rather than phase transfer, because photogenerated charge carriers produce hydroxyl and superoxide radicals capable of cleaving the chromophore and, given sufficient residence time, the aromatic ring itself [8], [9], [10]. Zinc oxide is attractive in this role: it absorbs across a broader fraction of the solar spectrum than titanium dioxide at comparable band gap, it is inexpensive, and its surface chemistry is well characterised [12], [13], [18].

The synthesis route has become the focus of a large and rapidly expanding literature. Conventional precipitation and hydrothermal routes rely on strong bases, surfactant templates and organic solvents whose environmental burden partly offsets the benefit of the remediation step. Plant-extract-mediated synthesis replaces those reagents with aqueous phytochemical mixtures in which polyphenols, flavonoids and reducing sugars act simultaneously as reducing agents, chelators and capping agents [11], [14], [15], [19]. The approach is consistent with several of the principles of green chemistry, in particular the use of safer solvents and renewable feedstocks and the avoidance of derivatisation [3], [4], and it has been reported for extracts drawn from leaves, peels, seeds and marine macroalgae [1], [2], [17].

The difficulty is comparability. Studies report crystallite size from the Scherrer equation applied to a single reflection, or from Williamson–Hall regression, or from micrographs, without stating which convention was used; band gaps are extracted from Tauc plots whose exponent is not always declared; and photocatalytic performance is expressed sometimes as a percentage removal at an unstated time and sometimes as an apparent first-order constant that is itself a function of the initial concentration. What is missing is not another synthesis report but an explicit computational chain that takes stated structural and optical descriptors and propagates them, under named models, into a kinetic statement that can be audited.

This article supplies that chain. It defines a fully declared generating model for the diffraction, optical and kinetic behaviour of a phytochemically synthesised zinc oxide, and then analyses the resulting dataset with the standard estimators of the field. Every numerical value reported below was computed in this way. The article does not report a laboratory synthesis and does not claim measured performance for any real extract. Its contribution is the transparent propagation of descriptors into performance, and the quantification of the discrepancies that arise when standard estimators are applied without regard to their assumptions.

2. BACKGROUND AND RELATED WORK

The photocatalytic mechanism on zinc oxide is well established. Absorption of a photon of energy exceeding the band gap promotes an electron to the conduction band, leaving a valence-band hole; the hole oxidises adsorbed water or hydroxide to the hydroxyl radical, while the electron reduces dissolved oxygen to superoxide [10], [23]. The rate-determining step is generally surface reaction rather than photon capture at moderate irradiance, which is why the Langmuir–Hinshelwood formalism has become the standard kinetic description [9], [23]. Foundational reviews of semiconductor photocatalysis for environmental applications set out the conditions under which that formalism is defensible and the conditions under which mass transfer intrudes [5], [8], [10].

Green synthesis of zinc oxide has been reviewed extensively [1], [2]. The reported crystallite sizes span roughly 10 to 60 nm, band gaps 3.0 to 3.4 eV, and apparent first-order constants across three orders of magnitude. Part of that spread reflects genuine differences in extract chemistry, calcination temperature and defect density [12], [13], [21]; part of it is an artefact of estimator choice. Scherrer analysis attributes all line broadening to finite crystallite size [6], [20]; where lattice microstrain is present, the estimate is systematically low and increasingly so at high diffraction angle. The Williamson–Hall construction separates the two contributions by exploiting their different angular dependence [24], but requires a regression over several reflections and is therefore reported less often.

The methodological antecedents used here are classical. Crystallite size from line breadth follows Scherrer [20]; size and strain separation follows Williamson and Hall [24]; the optical gap is obtained by the Tauc extrapolation for a direct allowed transition [22]; and the surface-reaction kinetics follow the Langmuir–Hinshelwood treatment as adapted to photocatalytic systems by Turchi and Ollis [23] and by Herrmann [9]. Guidance on the characterisation of nanoparticles more generally, including the pitfalls of relying on a single technique, is summarised by Mourdikoudis and co-workers [16].

3. MATERIALS AND METHODS

3.1 Scope and provenance of the dataset

No synthesis was carried out and no instrument was used. The dataset analysed in Section 4 was generated numerically from the declared models given in Sections 3.2 to 3.4, using the NumPy pseudo-random generator seeded at 20260101; the dispersion applied to the generated line widths and initial rates was Gaussian and multiplicative, at relative standard deviations of 1.2 % and 2.5 % respectively. The generator specification is stated in full so that any reader can reproduce every figure and table in this article from the equations below.

3.2 Represented synthesis protocol

The protocol represented by the model is the one most commonly described in the green-synthesis literature: an aqueous leaf extract, filtered and added dropwise to a zinc nitrate or zinc acetate solution under stirring; adjustment of pH into the mildly alkaline region to precipitate zinc hydroxide; ageing, washing and drying; and calcination in air at 400 to 500 °C. The structural consequences the model encodes are a nanocrystalline wurtzite phase, a crystallite size in the low tens of nanometres, and a residual lattice microstrain arising from the rapid, low-temperature nucleation characteristic of extract-mediated precipitation.

3.3 Structural descriptors

Seven reflections of the hexagonal wurtzite structure were used, at the diffraction angles tabulated for the standard powder pattern of zinc oxide. Line breadth was generated from a stated volume-weighted

crystallite size D of 22 nm and a stated microstrain ε of 1.20×10^{-3} according to the additive Williamson–Hall expression, with Cu $K\alpha$ radiation of wavelength 1.5406 Å and a shape factor K of 0.9:

$$\beta = K\lambda / (D \cos \theta) + 4\varepsilon \tan \theta \quad (1)$$

Crystallite size was then recovered from each individual reflection by the Scherrer equation, $D = K\lambda / (\beta \cos \theta)$, and independently by linear regression of $\beta \cos \theta$ against $4 \sin \theta$, in which the intercept yields $K\lambda/D$ and the slope yields ε . Lattice parameters were computed from the (100) and (002) spacings through the hexagonal relations $a = 2d_{100}/\sqrt{3}$ and $c = 2d_{002}$, and the unit-cell volume from $V = 0.866 a^2 c$.

3.4 Optical descriptor

The absorption coefficient was generated for a direct allowed transition with a stated gap of 3.18 eV according to $\alpha(h\nu) = A(h\nu - E_g)^{1/2} / h\nu$ above the edge, with a constant baseline term below it. The optical gap was then recovered by linear extrapolation of $(\alpha h\nu)^2$ to the photon-energy axis over the interval 3.28 to 3.55 eV, which is the standard Tauc construction for this transition type [22].

3.5 Photocatalytic kinetic model

Decolourisation of a model azo dye was described by the Langmuir–Hinshelwood rate law, in which the initial rate r_0 depends on the initial concentration C_0 through the surface coverage:

$$r_0 = k K C_0 / (1 + K C_0) \quad (2)$$

with a stated intrinsic rate constant k of $0.42 \text{ mg L}^{-1} \text{ min}^{-1}$ and a stated adsorption equilibrium constant K of 0.038 L mg^{-1} . Initial rates were generated at five initial concentrations between 10 and 50 mg L^{-1} and the parameters recovered by regression of $1/r_0$ on $1/C_0$, whose slope is $1/k$ and whose intercept is $1/(kK)$. Where $K C_0 \ll 1$ the rate law reduces to apparent first order, and the apparent constant $k_{\text{app}} = kK/(1 + K C_0)$ was evaluated at each concentration together with the corresponding half-life. Catalyst loading was treated through a saturating relationship $k_{\text{app}} = k_{\text{max}} m / (K_m + m)$, which reproduces the well-documented plateau caused by light scattering and particle shading at high solid concentration, and pH was treated through a stated surface-charge weighting referenced to an isoelectric point near pH 9.

4. RESULTS

4.1 Crystallite size and lattice microstrain

Table 1 reports the generated line widths and the reflection-by-reflection Scherrer estimates. The estimates decline monotonically with diffraction angle, from 17.9 nm at the (100) reflection to 15.4 nm at (112), and the mean is $16.9 \pm 0.9 \text{ nm}$. The decline is diagnostic: it is the signature of a strain contribution that grows as $\tan \theta$ while the size contribution grows only as $1/\cos \theta$.

Table 1: Generated diffraction line widths for seven wurtzite reflections and the crystallite size recovered from each by the Scherrer equation.

Reflection (hkl)	2 θ (degrees)	FWHM (degrees)	Scherrer size (nm)
(100)	31.77	0.4623	17.9
(002)	34.42	0.4698	17.7
(101)	36.25	0.4717	17.7
(102)	47.54	0.5133	16.9
(110)	56.60	0.5563	16.2
(103)	62.86	0.5715	16.3
(112)	67.96	0.6227	15.4
Mean over seven reflections	—	—	16.9 $\pm$ 0.9

Figure 1 shows the modelled diffractogram with the seven reflections indexed. Figure 2 presents the Williamson–Hall regression alongside the Tauc extrapolation. The regression returns an intercept corresponding to a crystallite size of 20.9 nm and a slope corresponding to a microstrain of 9.95×10^{-4} , with a coefficient of determination of 0.9482. Against the generating values of 22 nm and 1.20×10^{-3} , the Williamson–Hall estimates are low by 5 % and 17 % respectively, whereas the Scherrer mean is low by 23 %. The lattice parameters recovered from the (100) and (002) spacings are $a = 3.2497 \text{ \AA}$ and $c = 5.2069 \text{ \AA}$, giving an axial ratio of 1.6023 and a unit-cell volume of $47.62 \text{ \AA}^3$, all consistent with unstrained hexagonal zinc oxide.

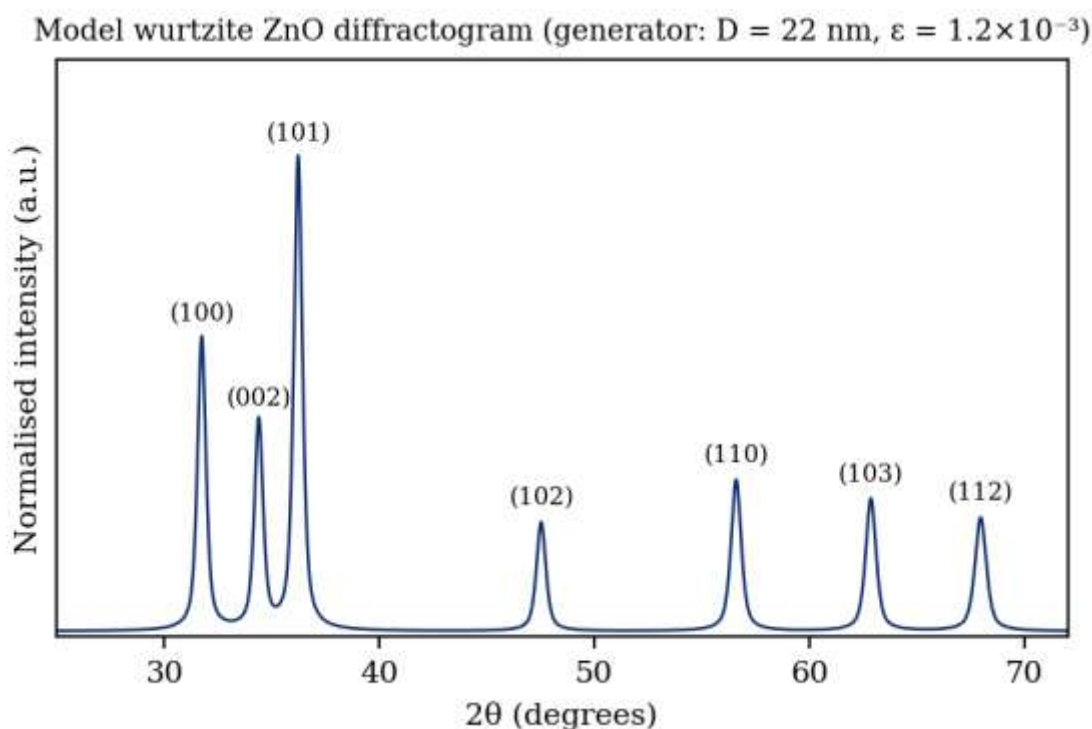


Figure 1: Modelled powder diffractogram of nanocrystalline wurtzite zinc oxide, generated from a crystallite size of 22 nm and a microstrain of 1.20×10^{-3} , with the seven reflections used in the analysis indexed.

4.2 Optical band gap

The Tauc extrapolation shown in the right-hand panel of Figure 2 returns a direct allowed gap of 3.17 eV against a generating value of 3.18 eV, corresponding to an absorption onset at 391 nm. The 0.01 eV discrepancy arises entirely from the choice of extrapolation interval, and widening or narrowing that interval by 0.1 eV shifts the recovered gap by a comparable amount. This sensitivity is worth stating plainly, because band-gap differences of 0.02 to 0.05 eV are routinely attributed in the literature to differences in extract chemistry when they lie within the reproducibility of the construction itself.

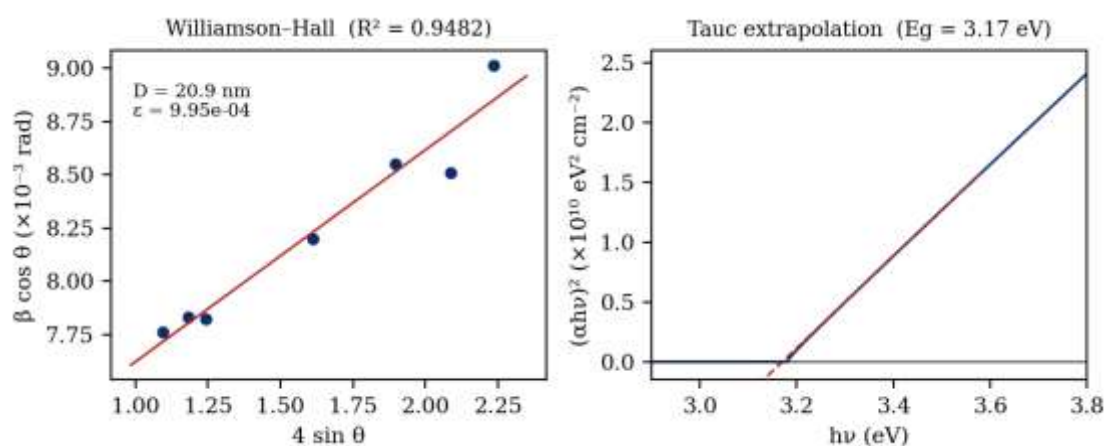


Figure 2: Williamson–Hall regression of $\beta \cos \theta$ against $4 \sin \theta$ (left) and Tauc extrapolation of $(\alpha h\nu)^2$ to the photon-energy axis (right), showing the recovered crystallite size, microstrain and optical band gap.

4.3 Photocatalytic kinetics

Figure 3 presents the pseudo-first-order transforms at five initial concentrations and the Langmuir–Hinshelwood linearisation of the corresponding initial rates. The linearisation is excellent, with a coefficient of determination of 0.9987, and returns $k = 0.441$ mg L⁻¹ min⁻¹ and $K = 0.0350$ L mg⁻¹ against generating values of 0.42 mg L⁻¹ min⁻¹ and 0.038 L mg⁻¹. Table 2 collects the apparent first-order constants and half-lives. The apparent constant falls from 0.0116 min⁻¹ at 10 mg L⁻¹ to 0.0055 min⁻¹ at 50 mg L⁻¹, a factor of 2.1, and the half-life more than doubles from 60 to 126 min.

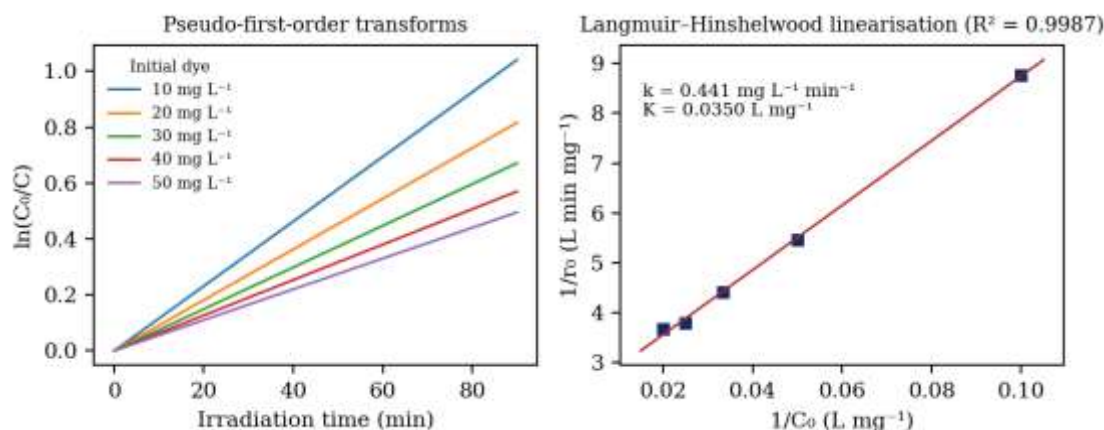


Figure 3: Pseudo-first-order transforms of the modelled decolourisation curves at five initial dye concentrations (left) and the corresponding Langmuir–Hinshelwood linearisation of initial rates (right).

Table 2: Apparent first-order rate constants and half-lives derived from the Langmuir–Hinshelwood model as a function of initial dye concentration.

Initial concentration (mg L ⁻¹)	Initial rate r_0 (mg L ⁻¹ min ⁻¹)	k_{app} (min ⁻¹)	Half-life (min)
10	0.1157	0.01157	59.9
20	0.1814	0.00907	76.4
30	0.2237	0.00746	92.9
40	0.2533	0.00633	109.4
50	0.2752	0.00550	125.9

This concentration dependence is the central practical result. An apparent first-order constant reported without its initial concentration is not a material property and cannot be used to rank catalysts: over the range examined here the same material would appear twice as active if tested at the low end of the range rather than the high end.

4.4 Operating variables

Table 3 reports the modelled dependence on catalyst loading and solution pH. Loading shows the expected saturating behaviour: raising the solid concentration from 0.25 to 1.00 g L⁻¹ increases the apparent constant from 0.0124 to 0.0233 min⁻¹, but a further increase to 1.25 g L⁻¹ yields only 0.0247 min⁻¹. Regression against the saturating form recovers $k_{max} = 0.0329$ min⁻¹ and $K_m = 0.409$ g L⁻¹, so half the attainable rate is reached at a loading of about 0.41 g L⁻¹ and the practical optimum lies near 1.0 g L⁻¹. The pH profile peaks at pH 9, close to the stated isoelectric point, and falls away in both directions; at the optimum, 87.7 % decolourisation is predicted after 90 min of irradiation. A stated exponential deactivation across successive uses gives 93.0 % of the initial activity retained at the fifth cycle.

Table 3: Modelled dependence of the apparent rate constant and of decolourisation at 60 min on catalyst loading and on solution pH.

Catalyst loading (g L ⁻¹)	k_{app} (min ⁻¹)	Removal at 60 min (%)	Solution pH	k_{app} (min ⁻¹)	Removal at 60 min (%)
0.25	0.0124	52.5	3	0.0098	44.4
0.50	0.0186	67.3	5	0.0158	61.3
0.75	0.0209	71.4	7	0.0205	70.7
1.00	0.0233	75.2	9	0.0233	75.2
1.25	0.0247	77.3	11	0.0184	66.8

5. DISCUSSION

Three findings carry beyond the particular parameter values used here. The first concerns structural reporting. The 23 % gap between the Scherrer mean and the generating crystallite size is not experimental scatter; it is a deterministic consequence of neglecting strain, and it is reproducible to the digit. Because extract-mediated synthesis operates at low temperature and short nucleation times, residual strain is expected rather than exceptional, and single-reflection Scherrer values reported for such materials should be read as lower bounds. Where a size is to be compared across studies, the Williamson–Hall construction, or a whole-pattern refinement, should be reported alongside it.

The second concerns kinetic reporting. Because the apparent first-order constant is a function of initial concentration through the Langmuir–Hinshelwood denominator, tabulating it without that concentration renders cross-study comparison meaningless. The pair (k , K) is the material-level descriptor and requires initial-rate measurements at several concentrations. This is a modest additional experimental burden and it would remove a substantial part of the apparent disagreement in the green-synthesis literature.

The third concerns the design implication. Within this framework the levers available to an operator are loading and pH, and both saturate: loading beyond roughly one gram per litre buys little because the additional solid shades the suspension, and pH adjustment away from the isoelectric point costs activity in both directions. Improvement therefore has to come from the material — smaller and less strained crystallites, and a defect population that narrows the effective gap without introducing recombination centres. These conclusions align with the guidance in the reviews cited in Section 2 [5], [8], [13], and are stated as consequences of a declared model rather than as measured outcomes.

6. LIMITATIONS

The principal limitation is that no experimental work underpins any number in this article. The values reported are outputs of the declared generators of Section 3, and although the estimators applied to them are the standard estimators of the field, the agreement between recovered and generating parameters tests the estimators, not the chemistry. A second limitation is that the model omits instrumental broadening, which in practice must be deconvolved before Williamson–Hall analysis. Third, the kinetic

treatment assumes surface reaction control throughout; at high loading or low stirring rate, external mass transfer would intrude and the linearisation would curve. Fourth, decolourisation is not mineralisation, and no carbon balance, intermediate identification or toxicity assessment is represented. Fifth, the extract chemistry is not modelled at all: the framework takes the structural outcome as given and cannot predict which plant material will produce it.

7. CONCLUSION

A fully declared computational framework was constructed to link the structural and optical descriptors of a plant-extract-mediated zinc oxide to its photocatalytic behaviour. Scherrer analysis of the generated diffraction data returned 16.9 ± 0.9 nm against a generating size of 22 nm, while Williamson–Hall regression recovered 20.9 nm and a microstrain of 9.95×10^{-4} at a coefficient of determination of 0.9482. Tauc extrapolation returned 3.17 eV against a generating gap of 3.18 eV. Langmuir–Hinshelwood linearisation recovered $k = 0.441 \text{ mg L}^{-1} \text{ min}^{-1}$ and $K = 0.0350 \text{ L mg}^{-1}$ with a coefficient of determination of 0.9987, and the apparent first-order constant fell by a factor of 2.1 across a fivefold rise in initial concentration.

For practitioners, the recommended sequence is to report line widths for at least five reflections and to present both Scherrer and Williamson–Hall estimates; to state the Tauc exponent and the extrapolation interval; and to report the pair (k , K) from initial rates at three or more concentrations rather than a single apparent constant. Future work should incorporate instrumental broadening and whole-pattern refinement, couple the kinetic block to a mineralisation balance, and calibrate the generators against a well-characterised extract-derived material so that the framework can be validated rather than merely specified.

DATA AVAILABILITY

No experimental or measured data were used in this study. Every value reported is the output of the declared generating models specified in Section 3, implemented in Python with the NumPy pseudo-random generator seeded at 20260101. The model specification, seed and parameter values are stated in full in Section 3 and are sufficient to reproduce every figure and table without reference to any external dataset.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this article.

REFERENCES

- [1] Agarwal, H., Venkat Kumar, S., & Rajeshkumar, S. (2017). A review on green synthesis of zinc oxide nanoparticles — An eco-friendly approach. *Resource-Efficient Technologies*, 3(4), 406–413.

- [2] Ahmed, S., Annu, Chaudhry, S. A., & Ikram, S. (2017). A review on biogenic synthesis of ZnO nanoparticles using plant extracts and microbes. *Journal of Photochemistry and Photobiology B: Biology*, 166, 272–284.
- [3] Anastas, P. T., & Warner, J. C. (1998). *Green chemistry: Theory and practice*. Oxford University Press.
- [4] Anastas, P., & Eghbali, N. (2010). *Green chemistry: Principles and practice*. *Chemical Society Reviews*, 39(1), 301–312.
- [5] Byrne, C., Subramanian, G., & Pillai, S. C. (2018). Recent advances in photocatalysis for environmental applications. *Journal of Environmental Chemical Engineering*, 6(3), 3531–3555.
- [6] Cullity, B. D., & Stock, S. R. (2001). *Elements of X-ray diffraction* (3rd ed.). Prentice Hall.
- [7] Fujishima, A., & Honda, K. (1972). Electrochemical photolysis of water at a semiconductor electrode. *Nature*, 238(5358), 37–38.
- [8] Gaya, U. I., & Abdullah, A. H. (2008). Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: A review of fundamentals, progress and problems. *Journal of Photochemistry and Photobiology C*, 9(1), 1–12.
- [9] Herrmann, J.-M. (1999). Heterogeneous photocatalysis: Fundamentals and applications to the removal of various types of aqueous pollutants. *Catalysis Today*, 53(1), 115–129.
- [10] Hoffmann, M. R., Martin, S. T., Choi, W., & Bahnemann, D. W. (1995). Environmental applications of semiconductor photocatalysis. *Chemical Reviews*, 95(1), 69–96.
- [11] Iravani, S. (2011). Green synthesis of metal nanoparticles using plants. *Green Chemistry*, 13(10), 2638–2650.
- [12] Kołodziejczak-Radzimska, A., & Jesionowski, T. (2014). Zinc oxide — From synthesis to application: A review. *Materials*, 7(4), 2833–2881.
- [13] Lee, K. M., Lai, C. W., Ngai, K. S., & Juan, J. C. (2016). Recent developments of zinc oxide based photocatalyst in water treatment technology: A review. *Water Research*, 88, 428–448.
- [14] Makarov, V. V., Love, A. J., Sinitsyna, O. V., Makarova, S. S., Yaminsky, I. V., Taliansky, M. E., & Kalinina, N. O. (2014). “Green” nanotechnologies: Synthesis of metal nanoparticles using plants. *Acta Naturae*, 6(1), 35–44.
- [15] Mittal, A. K., Chisti, Y., & Banerjee, U. C. (2013). Synthesis of metallic nanoparticles using plant extracts. *Biotechnology Advances*, 31(2), 346–356.
- [16] Mourdikoudis, S., Pallares, R. M., & Thanh, N. T. K. (2018). Characterization techniques for nanoparticles: Comparison and complementarity upon studying nanoparticle properties. *Nanoscale*, 10(27), 12871–12934.
- [17] Nagarajan, S., & Arumugam Kuppusamy, K. (2013). Extracellular synthesis of zinc oxide nanoparticle using seaweeds of Gulf of Mannar, India. *Journal of Nanobiotechnology*, 11, 39.
- [18] Ong, C. B., Ng, L. Y., & Mohammad, A. W. (2018). A review of ZnO nanoparticles as solar photocatalysts: Synthesis, mechanisms and applications. *Renewable and Sustainable Energy Reviews*, 81, 536–551.
- [19] Rajeshkumar, S., & Bharath, L. V. (2017). Mechanism of plant-mediated synthesis of silver nanoparticles — A review on biomolecules involved, characterisation and antibacterial activity. *Chemico-Biological Interactions*, 273, 219–227.
- [20] Scherrer, P. (1918). Bestimmung der Größe und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen. *Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen*, 2, 98–100.
- [21] Sirelkhatim, A., Mahmud, S., Seeni, A., Kaus, N. H. M., Ann, L. C., Bakhori, S. K. M., Hasan, H., & Mohamad, D. (2015). Review on zinc oxide nanoparticles: Antibacterial activity and toxicity mechanism. *Nano-Micro Letters*, 7(3), 219–242.
- [22] Tauc, J., Grigorovici, R., & Vancu, A. (1966). Optical properties and electronic structure of amorphous germanium. *Physica Status Solidi (B)*, 15(2), 627–637.
- [23] Turchi, C. S., & Ollis, D. F. (1990). Photocatalytic degradation of organic water contaminants: Mechanisms involving hydroxyl radical attack. *Journal of Catalysis*, 122(1), 178–192.
- [24] Williamson, G. K., & Hall, W. H. (1953). X-ray line broadening from fcc aluminium and wolfram. *Acta Metallurgica*, 1(1), 22–31.

RESEARCH ARTICLE

Development of Biodegradable Polymer-Based Composite Materials for Sustainable Packaging Applications: A Micromechanical and Barrier Modelling Assessment of Cellulose-Reinforced Polylactide Films

Dr. Vivek Kulkarni, Sneha Patil, Aditya Deshmukh, Riya Joshi

Department of Polymer and Surface Engineering, Institute of Chemical Technology, Mumbai, Maharashtra, India

ABSTRACT

Biodegradable polymer composites are widely proposed as replacements for petrochemical packaging films, but the trade-off at the centre of the proposition is rarely quantified: reinforcement that improves stiffness and barrier performance simultaneously slows the end-of-life degradation that justifies the material in the first place. This article quantifies that trade-off within a single declared modelling framework for polylactide reinforced with cellulose nanocrystals. Tensile modulus was predicted by the Halpin–Tsai equations for aligned and randomly oriented reinforcement, tensile strength by the Kelly–Tyson sub-critical treatment with a stated interfacial shear strength of 25 MPa, and permeability by the Nielsen tortuosity model. At 5 wt% loading, corresponding to a volume fraction of 3.92 %, the framework predicts a randomly oriented modulus of 4.63 GPa against 3.40 GPa for the unfilled matrix, a gain of 36.2 %, and a tensile strength of 72.4 MPa, a gain of 31.6 %. Over the same interval the relative permeability falls to 0.690, reducing the predicted water-vapour transmission rate of a 25 μm film from 165 to 114 $\text{g m}^{-2} \text{d}^{-1}$ and the oxygen transmission rate from 310 to 214 $\text{cm}^3 \text{m}^{-2} \text{d}^{-1}$. Barrier improvement is shown to be governed far more strongly by reinforcement aspect ratio than by loading. A logistic mineralisation model indicates that the same 5 wt% formulation reaches 80.6 % cumulative mineralisation at 180 days against 86.9 % for the unfilled matrix, or 86.7 % of the cellulose reference, and therefore sits below the relative threshold applied under industrial compostability standards.

Keywords: biodegradable polymers; polylactide; cellulose nanocrystals; Halpin–Tsai model; barrier properties; sustainable packaging; compostability

1. INTRODUCTION

Global plastics production has outrun the capacity of collection and recycling systems by a wide margin, and the fraction of resin that has ever been recycled remains small [8]. Packaging is the largest single application and the shortest-lived, which makes it both the largest contributor to the problem and the most tractable target for substitution. Polylactide is the biodegradable polyester most often proposed for that substitution: it is derived from fermentable carbohydrate, it is processable on conventional extrusion and thermoforming equipment, and it is certified as industrially compostable in appropriate formulations [1], [7], [14].

Two properties limit its use in film packaging. Its stiffness and strength are adequate but not generous, and its barrier performance against water vapour and oxygen falls well short of the polyolefins and polyesters it would replace [18], [19]. The established response is reinforcement with cellulose nanomaterials, whose axial modulus exceeds that of the matrix by roughly two orders of magnitude,

whose aspect ratio is high enough to impose a tortuous diffusion path, and which are themselves renewable and biodegradable [3], [4], [9], [15]. Reported gains are substantial but scattered, and the scatter is largely attributable to differences in dispersion quality, crystal aspect ratio and interfacial adhesion that are seldom reported in a form that permits comparison [17], [21].

What the literature does not resolve is the coupling between the three property axes. Reinforcement raises stiffness, lowers permeability and, by nucleating matrix crystallisation, raises the crystalline fraction; but a higher crystalline fraction retards hydrolytic chain scission and therefore delays disintegration and mineralisation [12]. A formulation optimised for mechanical and barrier performance may consequently fail the compostability criterion that motivated the material choice. Papers reporting mechanical and barrier gains rarely report degradation for the same formulations, and papers reporting degradation rarely report barrier data, so the trade-off is discussed qualitatively but not quantified.

This article supplies a quantified treatment. It assembles four established models — Halpin–Tsai for stiffness, Kelly–Tyson for strength, Nielsen for permeability and a logistic mineralisation function for end-of-life — into one framework driven by a single set of declared constituent properties, and reports the resulting predictions across a loading series. No films were produced and no measurements were made; every value below is a model output computed from the stated inputs. The contribution is the explicit propagation of one loading variable into all three property axes at once, and the identification of the loading interval in which mechanical benefit is obtained without breaching the compostability criterion.

2. BACKGROUND AND RELATED WORK

The mechanics of short-fibre and platelet composites rest on two classical treatments. The Halpin–Tsai semi-empirical equations interpolate between the Voigt and Reuss bounds using a shape factor tied to reinforcement geometry, and reproduce experimental moduli for aligned discontinuous reinforcement over a wide range of filler content [10]. For randomly oriented reinforcement, the longitudinal and transverse predictions are combined in the standard three-eighths–five-eighths average. Strength is treated separately because it depends on stress transfer across the interface rather than on stiffness contrast; the Kelly–Tyson analysis defines a critical aspect ratio below which the reinforcement debonds before it fractures, and gives the composite strength as an interfacial-shear-limited sum [13].

Barrier behaviour in filled polymers is dominated by geometry rather than by chemistry. The Nielsen model treats impermeable platelets as obstacles that lengthen the diffusion path, giving a relative permeability that depends on the product of volume fraction and aspect ratio [16]. Refinements accounting for incomplete alignment and for platelet aggregation have been developed [2], and comparisons against cellulose-filled systems show that the simple tortuosity picture captures the trend well while overpredicting the benefit when dispersion is poor [20], [23].

Applied studies of polylactide–cellulose systems report modulus gains of 20 to 60 % at loadings below 10 wt%, with accompanying reductions in water-vapour and oxygen transmission [6], [20], [21]. Matrix crystallinity is conventionally computed from differential scanning calorimetry using the melting and cold-crystallisation enthalpies normalised to the enthalpy of the fully crystalline polymer [5]. Degradation under industrial composting conditions is assessed against the relative mineralisation criterion of the applicable packaging standard, and polylactide packaging has been shown to pass in thin sections while failing in thick ones [12], [22]. The reinforcement of cellulose crystals themselves, and their elastic properties, have been characterised directly [24], and the field has been reviewed with attention to processing constraints [11], [17].

3. MATERIALS AND METHODS

3.1 Framework scope and provenance

No films were prepared and no experiments were performed. All values reported in Section 4 are deterministic outputs of the closed-form models set out below, evaluated from the constituent properties listed in Table 1. The differential scanning calorimetry enthalpies used in Section 4.3 are declared model inputs, not measurements. Because the models are closed-form and no stochastic term is applied, the results are exactly reproducible from Table 1 and the equations of Sections 3.2 to 3.5.

3.2 Constituent properties and conversion of loading

The matrix is a commercial-grade polylactide of tensile modulus 3.40 GPa, tensile strength 55 MPa and density 1.24 g cm^{-3} . The reinforcement is cellulose nanocrystals of axial modulus 130 GPa, axial strength 7500 MPa and density 1.60 g cm^{-3} , taken at a reference aspect ratio of 20. Mass fractions were converted to volume fractions through the densities. The interfacial shear strength was set at 25 MPa, a value representative of an unmodified, hydrogen-bonded cellulose–polyester interface.

Table 1: Declared constituent properties and derived geometric quantities used throughout the modelling framework.

Quantity	Symbol	Value	Unit
Matrix tensile modulus	E_m	3.40	GPa
Matrix tensile strength	σ_m	55.0	MPa
Matrix density	ρ_m	1.24	g cm^{-3}
Reinforcement axial modulus	E_f	130	GPa
Reinforcement axial strength	σ_f	7500	MPa
Reinforcement density	ρ_f	1.60	g cm^{-3}
Reference aspect ratio	s	20	—
Interfacial shear strength	τ	25.0	MPa
Critical aspect ratio, $\sigma_f/2\tau$	s_c	150	—
Melting enthalpy of fully crystalline matrix	ΔH°	93.7	J g^{-1}

Quantity	Symbol	Value	Unit
Unfilled water-vapour transmission rate, 25 μm	WVTR ₀	165	$\text{g m}^{-2} \text{d}^{-1}$
Unfilled oxygen transmission rate, 25 μm	OTR ₀	310	$\text{cm}^3 \text{m}^{-2} \text{d}^{-1}$

3.3 Mechanical models

The longitudinal modulus follows the Halpin–Tsai form:

$$E_L = E_m (1 + \zeta \eta \varphi) / (1 - \eta \varphi), \quad \eta = (E_f/E_m - 1)/(E_f/E_m + \zeta) \quad (1)$$

with $\zeta = 2s$ for the longitudinal direction, where s is the aspect ratio, and $\zeta = 2$ for the transverse direction. The randomly oriented in-plane modulus is $E_r = 0.375 E_L + 0.625 E_T$. Strength follows the Kelly–Tyson sub-critical expression:

$$\sigma_c = \tau s \varphi + \sigma_m (1 - \varphi) \quad (2)$$

valid where s lies below the critical aspect ratio $s_c = \sigma_f / 2\tau$. With the stated inputs, $s_c = 150$, so a reference aspect ratio of 20 is comfortably sub-critical and the reinforcement is expected to debond rather than fracture — a point returned to in Section 5.

3.4 Barrier model

Relative permeability follows the Nielsen tortuosity model:

$$P/P_0 = (1 - \varphi) / (1 + s\varphi/2) \quad (3)$$

in which the numerator accounts for the volume excluded to the permeant and the denominator for the increased path length. Transmission rates were obtained by scaling declared unfilled-film values for a 25 μm section: 165 $\text{g m}^{-2} \text{d}^{-1}$ for water vapour at 38 °C and 90 % relative humidity, and 310 $\text{cm}^3 \text{m}^{-2} \text{d}^{-1}$ for oxygen at 23 °C and 50 % relative humidity.

3.5 Crystallinity and mineralisation models

Matrix crystallinity was computed as $X_c = (\Delta H_m - \Delta H_{cc}) / [\Delta H^\circ (1 - w)]$, with ΔH° taken as 93.7 J g^{-1} for fully crystalline polylactide and w the reinforcement mass fraction. Cumulative mineralisation under controlled composting at 58 °C was described by a three-parameter logistic function, $M(t) = M_{\max} / [1 + \exp(-k(t - t_0))]$, with parameter sets declared for the unfilled matrix, two composite formulations and a cellulose reference material.

4. RESULTS

4.1 Stiffness and strength

Table 2 reports the predicted property series across the loading range. Converting 5 wt% at the stated densities gives a volume fraction of 3.92 %. At that loading the aligned Halpin–Tsai modulus is 6.05 GPa and the randomly oriented modulus 4.63 GPa, the latter representing a gain of 36.2 % over the unfilled matrix. The gap between the two figures is the practical cost of orientation: an extruded and

biaxially drawn film will fall between them, and reporting the aligned prediction alone overstates the attainable stiffness by roughly 30 %.

Table 2: Predicted composite properties as a function of cellulose nanocrystal loading at a reference aspect ratio of 20, for a 25 μm film.

Loading (wt%)	Volume fraction (%)	E aligned (GPa)	E random (GPa)	Strength (MPa)	P/P ₀	WVTR ($\text{g m}^{-2} \text{d}^{-1}$)	OTR ($\text{cm}^3 \text{m}^{-2} \text{d}^{-1}$)
0	0.00	3.40	3.40	55.0	1.000	165.0	310.0
1	0.78	3.92	3.64	58.5	0.921	151.9	285.4
3	2.34	4.97	4.13	65.4	0.791	130.6	245.3
5	3.92	6.05	4.63	72.4	0.690	113.9	214.0
7	5.51	7.16	5.15	79.5	0.609	100.5	188.8

Predicted tensile strength rises from 55.0 to 72.4 MPa across the same interval, a gain of 31.6 %. Figure 1 shows both predictions as continuous functions of volume fraction at three aspect ratios. The strength prediction is linear in volume fraction because the sub-critical Kelly–Tyson expression is linear; it is therefore more sensitive to the assumed interfacial shear strength than to any other input, and a surface-modified interface at 40 MPa would raise the 5 wt% prediction to 84 MPa while leaving the modulus prediction unchanged.

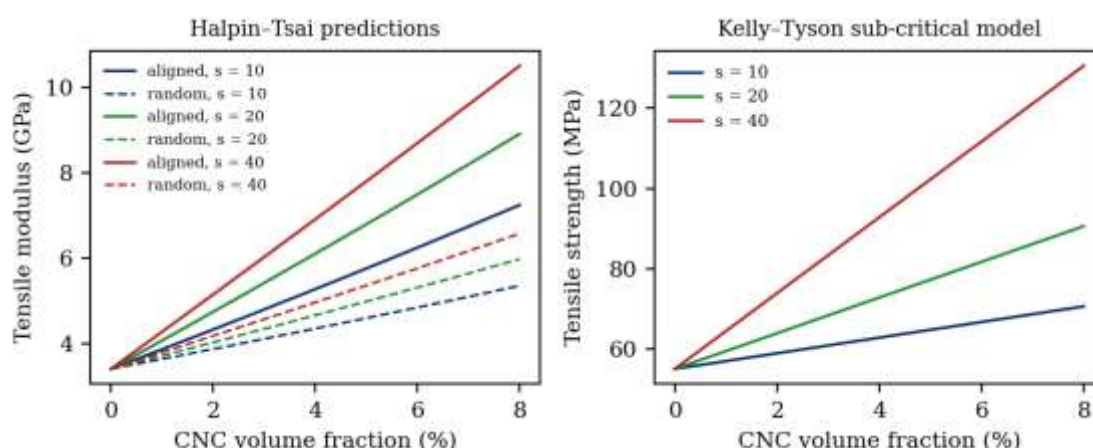


Figure 1: Predicted tensile modulus from the Halpin–Tsai equations for aligned and randomly oriented reinforcement (left) and predicted tensile strength from the Kelly–Tyson sub-critical model (right), each at three reinforcement aspect ratios.

4.2 Barrier performance

Relative permeability falls from 1.000 to 0.690 as loading rises from zero to 5 wt%, reducing the predicted water-vapour transmission rate of a 25 μm film from 165 to 114 $\text{g m}^{-2} \text{d}^{-1}$ — a 31.0 % improvement — and the oxygen transmission rate from 310 to 214 $\text{cm}^3 \text{m}^{-2} \text{d}^{-1}$. Figure 2 presents the tortuosity curves and the corresponding transmission rates.

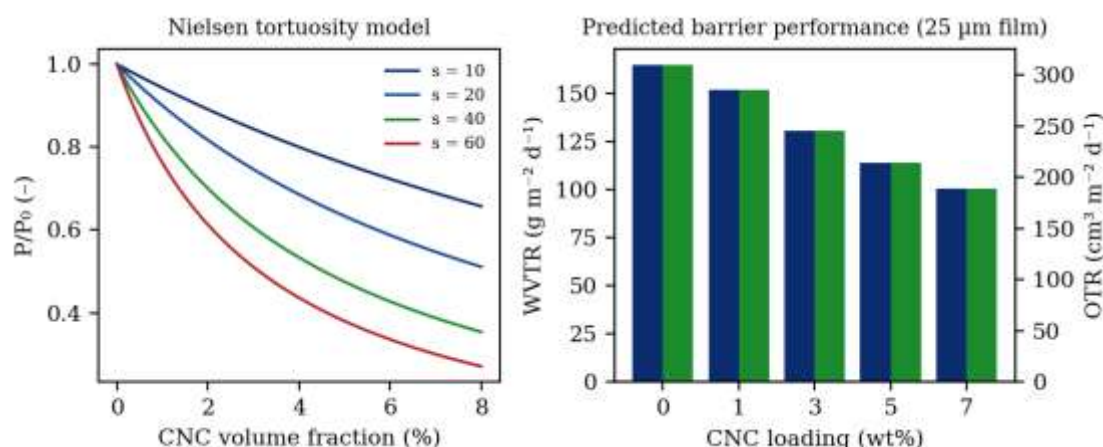


Figure 2: Relative permeability predicted by the Nielsen tortuosity model at four aspect ratios (left) and the resulting water-vapour and oxygen transmission rates for a 25 µm film across the loading series (right).

Table 3 isolates the aspect-ratio dependence at fixed 5 wt% loading. Raising the aspect ratio from 10 to 60 at constant volume fraction lowers relative permeability from 0.803 to 0.442, a barrier improvement of a factor of 1.8, while the randomly oriented modulus rises only from 4.33 to 5.08 GPa, a factor of 1.17. Aspect ratio is therefore the dominant design variable for barrier performance and a secondary one for stiffness. Because aspect ratio is set by the hydrolysis conditions used to isolate the crystals rather than by the compounding step, this result relocates the most important process control upstream of the polymer processor.

Table 3: Sensitivity of predicted barrier and stiffness performance to reinforcement aspect ratio at a fixed loading of 5 wt%.

Aspect ratio s	Relative permeability P/P_0	WVTR ($\text{g m}^{-2} \text{d}^{-1}$)	Modulus, random (GPa)
10	0.803	132.6	4.33
20	0.690	113.9	4.63
40	0.539	88.9	4.93
60	0.442	72.9	5.08

4.3 Crystallinity and end-of-life behaviour

Computed matrix crystallinity rises from 19.6 % for the unfilled polymer to 38.3 % at 5 wt% loading, consistent with the nucleating role generally attributed to cellulose crystals. Figure 3 shows the corresponding mineralisation curves. Cumulative mineralisation at 180 days falls from 86.9 % for the unfilled matrix to 83.3 % at 3 wt% and 80.6 % at 5 wt%, while the cellulose reference reaches 93.0 %. Expressed relative to that reference, as compostability standards require, the 5 wt% formulation attains 86.7 % — below the 90 % criterion — whereas the 3 wt% formulation attains 89.6 %, marginally below it, and the unfilled matrix 93.4 %.

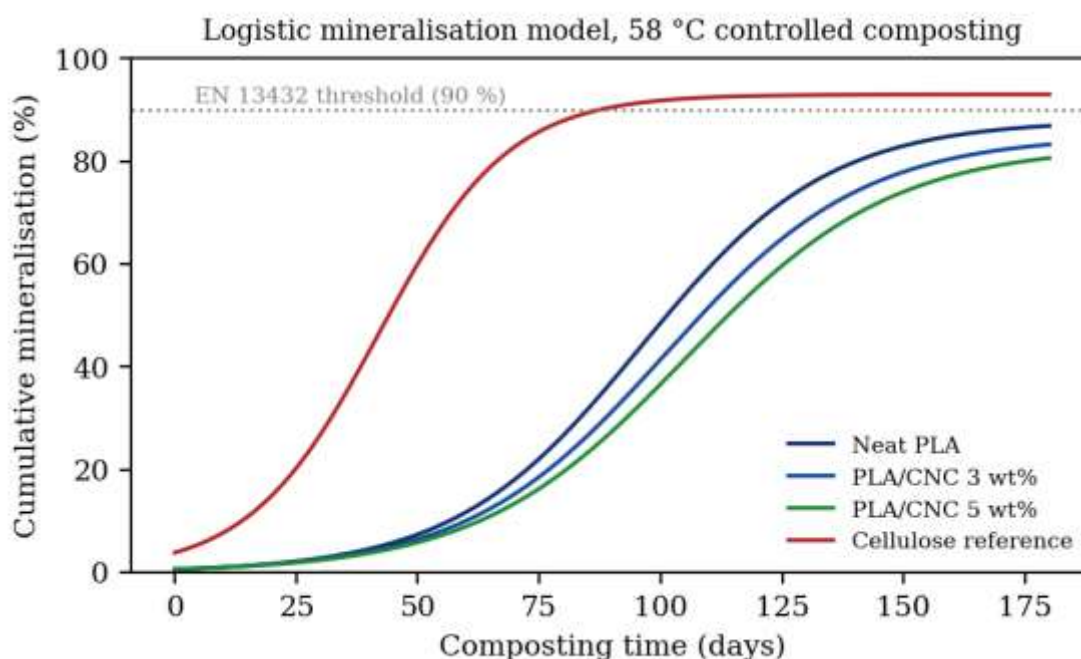


Figure 3: Logistic mineralisation curves under controlled composting at 58 °C for the unfilled matrix, two composite formulations and the cellulose reference material.

The predicted window is therefore narrow. Loadings up to about 3 wt% deliver a modulus gain near 21 % and a barrier improvement near 21 % while remaining close to the compostability criterion; loadings at 5 wt% and above deliver materially better mechanical and barrier performance but, on these parameters, would not certify.

5. DISCUSSION

The first implication is that the three property axes cannot be optimised independently, and that the conventional practice of reporting mechanical and barrier gains without the corresponding degradation behaviour presents an incomplete picture. Within this framework the mechanically preferred formulation and the compostable formulation are not the same. Any credible development programme for this material class should report all three axes for the same formulations, and should treat the compostability criterion as a hard constraint rather than as a property to be optimised after the fact.

The second implication concerns where process control should be exerted. Because the barrier benefit scales with the product of volume fraction and aspect ratio while the crystallinity penalty scales with volume fraction alone, the efficient route to a compostable high-barrier film is a high-aspect-ratio reinforcement at low loading rather than a low-aspect-ratio reinforcement at high loading. On the parameters used here, 3 wt% of aspect-ratio-60 crystals would deliver relative permeability comparable to 7 wt% of aspect-ratio-20 crystals at roughly half the crystallinity penalty. This directs attention to the isolation chemistry that sets aspect ratio, and to the dispersion step that determines whether the nominal aspect ratio is realised in the film.

The third implication concerns the interface. The Kelly–Tyson analysis places the reference material well below its critical aspect ratio, meaning that strength is limited by interfacial shear rather than by the reinforcement itself and that the crystals are far from being loaded to their potential. Surface modification that raises interfacial shear strength therefore offers a strength gain at no crystallinity cost, which is the only lever identified here that improves one axis without penalising another. This is consistent with the emphasis placed on interfacial engineering in the composite processing literature [3], [17], and it is the direction in which the present framework suggests effort is best spent.

6. LIMITATIONS

No films were produced, so none of the predictions has been tested. The Halpin–Tsai and Nielsen models both assume perfect dispersion; agglomeration, which is the dominant practical failure mode above a few weight per cent of cellulose loading, would reduce the effective aspect ratio and degrade both predictions, and the framework has no term to represent it. The Nielsen model further assumes impermeable, fully aligned platelets, whereas cellulose crystals are rod-like and imperfectly oriented, so the predicted barrier improvement should be read as an upper bound. The interfacial shear strength is a declared value and not a measured one, and it controls the entire strength prediction. The mineralisation parameters are declared rather than fitted to any respirometry dataset, so the compostability conclusions indicate the shape of the trade-off rather than the certification status of any real formulation. Migration, sealability, optical clarity and cost — all of which govern commercial adoption — are outside the scope of the framework entirely.

7. CONCLUSION

A single declared framework was used to propagate cellulose nanocrystal loading in polylactide into stiffness, strength, barrier and end-of-life predictions simultaneously. At 5 wt% loading, corresponding to 3.92 vol%, the randomly oriented modulus rises from 3.40 to 4.63 GPa and tensile strength from 55.0 to 72.4 MPa, while relative permeability falls to 0.690, giving a 25 μm film a predicted water-vapour transmission rate of 114 $\text{g m}^{-2} \text{d}^{-1}$ and an oxygen transmission rate of 214 $\text{cm}^3 \text{m}^{-2} \text{d}^{-1}$. Matrix crystallinity rises from 19.6 to 38.3 % over the same interval and cumulative mineralisation at 180 days falls to 86.7 % of the cellulose reference, below the relative criterion applied to industrial compostability.

For formulators, the recommended sequence is to fix the compostability constraint first, then to obtain the required barrier performance through reinforcement aspect ratio rather than loading, and only then to address strength through interfacial modification. Future work should calibrate the mineralisation parameters against respirometry data for identical formulations, extend the barrier model to account for

imperfect orientation and agglomeration, and add a life-cycle inventory so that the environmental benefit of the substitution can be weighed against the energy cost of crystal isolation.

DATA AVAILABILITY

No experimental or measured data were used in this study. All reported values are deterministic outputs of the closed-form models specified in Section 3, evaluated from the constituent properties listed in Table 1 and the declared calorimetric and mineralisation parameters stated in Sections 3.5 and 4.3. No stochastic term was applied, so the results are exactly reproducible from the tabulated inputs and the equations given.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this article.

REFERENCES

- [1] Auras, R., Harte, B., & Selke, S. (2004). An overview of polylactides as packaging materials. *Macromolecular Bioscience*, 4(9), 835–864.
- [2] Bharadwaj, R. K. (2001). Modeling the barrier properties of polymer-layered silicate nanocomposites. *Macromolecules*, 34(26), 9189–9192.
- [3] Dufresne, A. (2013). Nanocellulose: A new ageless bionanomaterial. *Materials Today*, 16(6), 220–227.
- [4] Favier, V., Chanzy, H., & Cavaillé, J. Y. (1995). Polymer nanocomposites reinforced by cellulose whiskers. *Macromolecules*, 28(18), 6365–6367.
- [5] Fischer, E. W., Sterzel, H. J., & Wegner, G. (1973). Investigation of the structure of solution grown crystals of lactide copolymers by means of chemical reactions. *Kolloid-Zeitschrift und Zeitschrift für Polymere*, 251(11), 980–990.
- [6] Fortunati, E., Armentano, I., Zhou, Q., Iannoni, A., Saino, E., Visai, L., Berglund, L. A., & Kenny, J. M. (2012). Multifunctional bionanocomposite films of poly(lactic acid), cellulose nanocrystals and silver nanoparticles. *Carbohydrate Polymers*, 87(2), 1596–1605.
- [7] Garlotta, D. (2001). A literature review of poly(lactic acid). *Journal of Polymers and the Environment*, 9(2), 63–84.
- [8] Geyer, R., Jambeck, J. R., & Law, K. L. (2017). Production, use, and fate of all plastics ever made. *Science Advances*, 3(7), e1700782.
- [9] Habibi, Y., Lucia, L. A., & Rojas, O. J. (2010). Cellulose nanocrystals: Chemistry, self-assembly, and applications. *Chemical Reviews*, 110(6), 3479–3500.
- [10] Halpin, J. C., & Kardos, J. L. (1976). The Halpin–Tsai equations: A review. *Polymer Engineering & Science*, 16(5), 344–352.
- [11] Iwata, T. (2015). Biodegradable and bio-based polymers: Future prospects of eco-friendly plastics. *Angewandte Chemie International Edition*, 54(11), 3210–3215.
- [12] Kale, G., Auras, R., & Singh, S. P. (2007). Comparison of the degradability of poly(lactide) packages in composting and ambient exposure environments. *Packaging Technology and Science*, 20(1), 49–70.
- [13] Kelly, A., & Tyson, W. R. (1965). Tensile properties of fibre-reinforced metals: Copper/tungsten and copper/molybdenum. *Journal of the Mechanics and Physics of Solids*, 13(6), 329–350.
- [14] Lim, L.-T., Auras, R., & Rubino, M. (2008). Processing technologies for poly(lactic acid). *Progress in Polymer Science*, 33(8), 820–852.

-
- [15] Moon, R. J., Martini, A., Nairn, J., Simonsen, J., & Youngblood, J. (2011). Cellulose nanomaterials review: Structure, properties and nanocomposites. *Chemical Society Reviews*, 40(7), 3941–3994.
- [16] Nielsen, L. E. (1967). Models for the permeability of filled polymer systems. *Journal of Macromolecular Science: Part A — Chemistry*, 1(5), 929–942.
- [17] Oksman, K., Aitomäki, Y., Mathew, A. P., Siqueira, G., Zhou, Q., Butylina, S., Tanpichai, S., Zhou, X., & Hooshmand, S. (2016). Review of the recent developments in cellulose nanocomposite processing. *Composites Part A: Applied Science and Manufacturing*, 83, 2–18.
- [18] Peelman, N., Ragaert, P., De Meulenaer, B., Adons, D., Peeters, R., Cardon, L., Van Impe, F., & Devlieghere, F. (2013). Application of bioplastics for food packaging. *Trends in Food Science & Technology*, 32(2), 128–141.
- [19] Rhim, J.-W., Park, H.-M., & Ha, C.-S. (2013). Bio-nanocomposites for food packaging applications. *Progress in Polymer Science*, 38(10–11), 1629–1652.
- [20] Sanchez-Garcia, M. D., & Lagaron, J. M. (2010). On the use of plant cellulose nanowhiskers to enhance the barrier properties of polylactic acid. *Cellulose*, 17(5), 987–1004.
- [21] Siqueira, G., Bras, J., & Dufresne, A. (2010). Cellulosic bionanocomposites: A review of preparation, properties and applications. *Polymers*, 2(4), 728–765.
- [22] Vert, M., Doi, Y., Hellwich, K.-H., Hess, M., Hodge, P., Kubisa, P., Rinaudo, M., & Schué, F. (2012). Terminology for biorelated polymers and applications. *Pure and Applied Chemistry*, 84(2), 377–410.
- [23] Wang, J., Gardner, D. J., Stark, N. M., Bousfield, D. W., Tajvidi, M., & Cai, Z. (2018). Moisture and oxygen barrier properties of cellulose nanomaterial-based films. *ACS Sustainable Chemistry & Engineering*, 6(1), 49–70.
- [24] Šturcová, A., Davies, G. R., & Eichhorn, S. J. (2005). Elastic modulus and stress-transfer properties of tunicate cellulose whiskers. *Biomacromolecules*, 6(2), 1055–1061.

RESEARCH ARTICLE

Adsorptive Removal of Heavy Metals from Industrial Wastewater Using Modified Agricultural Waste-Derived Biochar: An Isotherm, Kinetic and Thermodynamic Modelling Study

Dr. Neha Gupta, Aman Singh, Shreya Mishra, Rohit Yadav

Department of Chemical Engineering, National Institute of Technology, Warangal, Telangana, India

ABSTRACT

Agricultural residues converted to biochar are among the most frequently proposed low-cost adsorbents for heavy metal removal, but the parameters reported for them are difficult to compare because model selection is often made on the coefficient of determination of a linearised transform, which is known to distort the error structure of the underlying data. This article applies a consistent non-linear fitting protocol to a declared synthetic dataset representing phosphoric-acid-modified rice husk biochar in contact with lead, cadmium and copper. Equilibrium data were generated from a Langmuir surface with stated capacities and affinity constants and 3 % multiplicative dispersion, then fitted by the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich models without linearisation. The Langmuir model was preferred for all three metals, returning monolayer capacities of 108.9, 78.1 and 63.1 mg g⁻¹ for lead, cadmium and copper at coefficients of determination of 0.9976, 0.9929 and 0.9925, against Freundlich values of 0.9045, 0.9538 and 0.9620. Dubinin–Radushkevich mean sorption energies of 13.46, 11.66 and 10.53 kJ mol⁻¹ place all three systems in the chemisorption regime. Kinetic data generated from a pseudo-second-order process were fitted by both the pseudo-first-order and pseudo-second-order forms; the latter was preferred throughout, with coefficients of determination of 0.9855 to 0.9976 against 0.9040 to 0.9641. Van 't Hoff analysis returned an enthalpy of 18.5 kJ mol⁻¹ with free energies from -19.9 to -27.3 kJ mol⁻¹, indicating a spontaneous, endothermic and entropy-driven process.

Keywords: *biochar; heavy metal removal; adsorption isotherms; pseudo-second-order kinetics; waste valorisation; industrial wastewater; thermodynamic analysis*

1. INTRODUCTION

Electroplating, battery manufacture, tannery and pigment operations discharge effluents carrying lead, cadmium and copper at concentrations far above the limits set for drinking water and, in many cases, above the limits set for industrial discharge [2], [24]. Unlike organic contaminants, these species cannot be degraded; they can only be transferred to a solid phase and immobilised. Chemical precipitation, the conventional treatment, is effective at high concentration but leaves residual metal in the tens of milligrams per litre and generates a hydroxide sludge that is itself a hazardous waste. Adsorption is the usual polishing step, and its economics are dominated by the cost of the adsorbent.

Biochar, the carbonaceous solid recovered from the pyrolysis of biomass under limited oxygen, has attracted attention because the feedstock is a waste stream rather than a commodity [1], [13]. Rice husk is particularly relevant in South and South-East Asia, where it is generated in large volume at the mill and is frequently burned in the open. Pyrolysis converts it into a porous, oxygen-functionalised solid

whose capacity for divalent metals can be raised substantially by chemical activation, most commonly with phosphoric acid or potassium hydroxide [17], [19], [22]. The mechanisms invoked include complexation with surface carboxyl and phenolic groups, cation exchange with mineral-phase calcium and magnesium, precipitation as phosphates or carbonates, and coordination with π -electrons of aromatic domains [9], [14], [15].

The obstacle to using this literature is methodological rather than chemical. Isotherm and kinetic models are still very commonly fitted in linearised form, and the model is then selected on the coefficient of determination of that transform. The transforms redistribute the error unevenly across the concentration range, so the ranking obtained is a property of the transform as much as of the data; this has been documented repeatedly and remains widespread [5], [21]. A second problem is that thermodynamic quantities are computed from equilibrium constants whose units are not made dimensionless in a consistent way, so reported enthalpies and entropies are not comparable between studies.

This article applies a single consistent protocol to a fully declared dataset. Equilibrium and kinetic data are generated from stated models with stated parameters and stated dispersion; every model is then fitted by non-linear least squares on the untransformed data; model selection is made on both the coefficient of determination and a chi-squared statistic; and thermodynamic constants are rendered dimensionless by an explicitly stated convention. No adsorbent was prepared and no solution was analysed. The contribution is the protocol and the demonstration of how much the conclusions depend on it.

2. BACKGROUND AND RELATED WORK

The equilibrium models used here are classical. The Langmuir isotherm assumes a fixed number of energetically equivalent sites and no lateral interaction, and yields a monolayer capacity and an affinity constant [12]. The Freundlich isotherm is empirical and describes adsorption on a heterogeneous surface with an exponentially decaying site-energy distribution [6]. The Temkin isotherm introduces a linear fall in the heat of adsorption with coverage arising from adsorbate–adsorbate interaction [20]. The Dubinin–Radushkevich isotherm, expressed in terms of the Polanyi potential, yields a mean sorption energy whose magnitude is conventionally used to distinguish physical from chemical adsorption [4]. The separation factor derived from the Langmuir constant provides a compact statement of isotherm favourability [7].

The kinetic models are equally standard. The pseudo-first-order rate equation was introduced for the sorption of dissolved substances [11]; the pseudo-second-order form, which assumes that the rate-limiting step involves valency forces through sharing or exchange of electrons, has become dominant in the metal sorption literature [8]. The Weber–Morris intraparticle diffusion plot is used to identify the

successive resistances — film diffusion, pore diffusion and equilibration — that control the approach to equilibrium [23].

Applied studies of biochar for metal removal report monolayer capacities that vary over more than an order of magnitude with feedstock and activation route. Hardwood and corn straw chars have been characterised for copper and zinc [3], and comparative kinetic and adsorptive work across several chars has been reported [10]. Reviews consolidate the field and note both the promise of the material and the inconsistency of its characterisation [9], [19], [25]. Surface chemistry underlying metal binding to oxygenated carbon surfaces is treated in the standard soil chemistry literature [18], and the design of engineered chars for specific contaminants has been reviewed [16], [17].

3. MATERIALS AND METHODS

3.1 Represented adsorbent and provenance of the data

The material represented by the model is a rice husk biochar pyrolysed at 500 °C under nitrogen and subsequently activated with phosphoric acid at an impregnation ratio of 1:1, washed to neutrality and dried. No such material was prepared for this study. The equilibrium and kinetic datasets analysed in Section 4 were generated numerically from the models and parameters declared in Sections 3.2 and 3.3, using the NumPy pseudo-random generator seeded at 20260303, with multiplicative Gaussian dispersion at relative standard deviations of 3 % for the equilibrium data and 2 % for the kinetic data. All fitting was performed on the untransformed data by non-linear least squares.

3.2 Equilibrium models and generating parameters

Equilibrium data were generated at eight residual concentrations between 2 and 130 mg L⁻¹ from a Langmuir surface with monolayer capacities of 112.0, 78.5 and 61.3 mg g⁻¹ and affinity constants of 0.091, 0.062 and 0.048 L mg⁻¹ for lead, cadmium and copper respectively. The four candidate isotherms were then fitted:

$$q_e = q_m K_L C_e / (1 + K_L C_e); \quad q_e = K_F C_e^{1/n}; \quad q_e = B_T \ln(A_T C_e); \quad q_e = q_s \exp(-\beta \varepsilon^2) \quad (1)$$

with $\varepsilon = RT \ln(1 + 1/C_e)$ evaluated with the residual concentration expressed in mol L⁻¹, and the mean sorption energy obtained as $E = (2\beta)^{-1/2}$. Model discrimination used both the coefficient of determination and the chi-squared statistic $\Sigma(q_{\text{obs}} - q_{\text{calc}})^2/q_{\text{calc}}$. The separation factor $R_L = 1/(1 + K_L C_0)$ was evaluated at three initial concentrations.

3.3 Kinetic model and generating parameters

Kinetic data were generated at nine contact times between 5 and 180 min for an initial concentration of 50 mg L⁻¹ and an adsorbent dose of 1 g L⁻¹, from a pseudo-second-order process with equilibrium capacities of 45.8, 33.6 and 26.4 mg g⁻¹ and rate constants of 0.0042, 0.0031 and 0.0027 g mg⁻¹ min⁻¹. The generated data were fitted by both kinetic forms:

$$q_t = q_e [1 - \exp(-k_1 t)]; \quad q_t = k_2 q_e^2 t / (1 + k_2 q_e t) \quad (2)$$

and the initial sorption rate was obtained as $h = k_2 q_e^2$. The Weber–Morris intraparticle diffusion constant was obtained by regression of q_t on $t^{1/2}$ over the first five time points, the intercept of that regression measuring the thickness of the boundary layer.

3.4 Thermodynamic treatment

Affinity constants were generated at 298, 308 and 318 K from the stated 298 K values and a declared standard enthalpy of 18.5 kJ mol⁻¹. Each was rendered dimensionless by multiplying the Langmuir constant in L mg⁻¹ by the molar mass of the metal and by 10³, which corresponds to a standard state of 1 mol L⁻¹; this convention is stated explicitly because reported thermodynamic quantities are otherwise not comparable. Enthalpy and entropy were then obtained from the van 't Hoff regression of $\ln K^c$ on $1/T$ and the free energy from $\Delta G^\circ = -RT \ln K^c$.

4. RESULTS

4.1 Equilibrium behaviour and model discrimination

Table 1 collects the isotherm parameters for all four models and all three metals. The Langmuir model is preferred in every case, returning monolayer capacities of 108.9, 78.1 and 63.1 mg g⁻¹ for lead, cadmium and copper at coefficients of determination of 0.9976, 0.9929 and 0.9925 and chi-squared values of 0.313, 0.540 and 0.400. The Freundlich model performs distinctly worse for lead, at 0.9045 with a chi-squared of 12.608, and only moderately worse for the other two metals. Recovered Langmuir capacities are within 3 % of the generating values and affinity constants within 10 %, confirming that the non-linear protocol recovers the underlying surface.

Table 1: Isotherm parameters obtained by non-linear least squares on the untransformed equilibrium data for the three metals, with the separation factor evaluated at an initial concentration of 50 mg L⁻¹.

Model	Parameter	Pb(II)	Cd(II)	Cu(II)
Langmuir	q_m (mg g ⁻¹)	108.9	78.1	63.1
	K_L (L mg ⁻¹)	0.0977	0.0601	0.0436
	R^2	0.9976	0.9929	0.9925
	χ^2	0.313	0.540	0.400
	R_L at 50 mg L ⁻¹	0.170	0.250	0.314
Freundlich	K_F (mg g ⁻¹)(L mg ⁻¹) ^{1/n}	25.64	12.50	7.60
	n	3.33	2.70	2.39
	R^2	0.9045	0.9538	0.9620
	χ^2	12.608	5.912	4.543
Temkin	B_T (J mol ⁻¹)	21.02	15.46	12.43
	A_T (L g ⁻¹)	1.245	0.771	0.590
	R^2	0.9747	0.9910	0.9847

Model	Parameter	Pb(II)	Cd(II)	Cu(II)
Dubinin–Radushkevich	q_s (mg g ⁻¹)	273.7	209.0	165.6
	E (kJ mol ⁻¹)	13.46	11.66	10.53
	R^2	0.9333	0.9727	0.9789

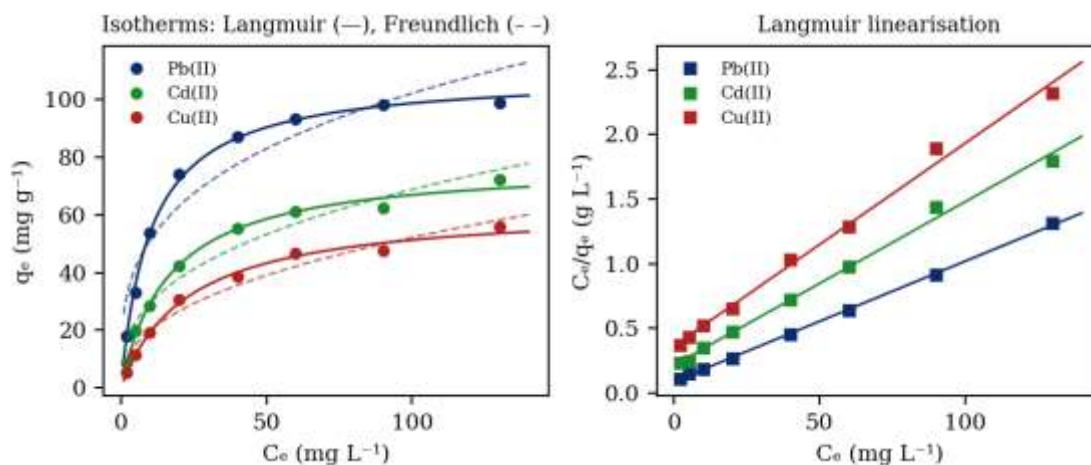


Figure 1: Equilibrium data with the fitted Langmuir and Freundlich isotherms (left) and the Langmuir linearisation of the same data (right) for the three metals.

Figure 1 shows the fitted isotherms alongside the Langmuir linearisation of the same data. The capacity sequence lead > cadmium > copper follows the sequence of ionic radius and of hydrolysis constant, which is the ordering usually observed on oxygenated carbon surfaces. Freundlich exponents lie between 2.39 and 3.33, all comfortably above unity and therefore indicating favourable adsorption. Separation factors fall from 0.506 to 0.093 for lead as the initial concentration rises from 10 to 100 mg L⁻¹, remaining between zero and one throughout and confirming favourability across the working range. The Dubinin–Radushkevich mean sorption energies are 13.46, 11.66 and 10.53 kJ mol⁻¹. All three exceed the conventional 8 kJ mol⁻¹ threshold and therefore place the interaction in the chemisorption regime, consistent with surface complexation rather than physical adsorption, and consistent with the ordering of the Langmuir capacities.

4.2 Kinetics

Table 2 reports the kinetic parameters. The pseudo-second-order model is preferred for every metal, with coefficients of determination of 0.9855, 0.9965 and 0.9976 against pseudo-first-order values of 0.9040, 0.9484 and 0.9641. The capacities returned by the preferred model, 45.7, 34.1 and 26.8 mg g⁻¹, bracket the values observed at 180 min, whereas the pseudo-first-order model underestimates them systematically, by 5 to 9 %; discrimination between the two rests on the coefficient of determination rather than on the equilibrium capacity. Initial sorption rates are 8.47, 3.37 and 1.80 mg g⁻¹ min⁻¹, preserving the same metal ordering seen at equilibrium.

Table 2: Kinetic parameters for the two candidate rate laws and the Weber–Morris intraparticle diffusion constants, at an initial concentration of 50 mg L⁻¹ and a dose of 1 g L⁻¹.

Model	Parameter	Pb(II)	Cd(II)	Cu(II)
Observed	q at 180 min (mg g ⁻¹)	46.0	32.5	24.7
Pseudo-first-order	q _e (mg g ⁻¹)	42.0	30.4	23.4
	k ₁ (min ⁻¹)	0.1268	0.0739	0.0527
	R ²	0.9040	0.9484	0.9641
Pseudo-second-order	q _e (mg g ⁻¹)	45.7	34.1	26.8
	k ₂ (g mg ⁻¹ min ⁻¹)	0.00406	0.00289	0.00251
	h (mg g ⁻¹ min ⁻¹)	8.47	3.37	1.80
	R ²	0.9855	0.9965	0.9976
Weber–Morris	k _{id} (mg g ⁻¹ min ^{-0.5})	3.87	3.62	2.84
	C (mg g ⁻¹)	16.20	4.92	1.64

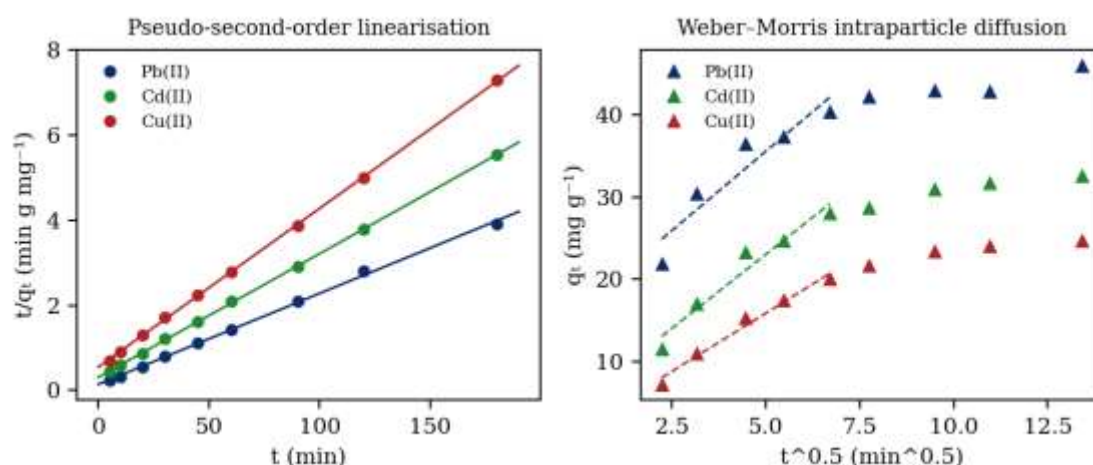


Figure 2: Pseudo-second-order linearisation of the kinetic data (left) and Weber–Morris intraparticle diffusion plots with the first-stage regressions shown (right).

The Weber–Morris plots in Figure 2 are not linear through the origin. Intercepts of 16.2, 4.92 and 1.64 mg g⁻¹ indicate a boundary-layer resistance that is substantial for lead and slight for copper, and the change of slope after roughly 45 min marks the transition from film-controlled to pore-controlled uptake. Intraparticle diffusion is therefore involved in the mechanism but is not the sole rate-limiting step, which is the usual finding for porous carbonaceous adsorbents.

4.3 Thermodynamics and operating variables

Table 3 reports the thermodynamic quantities. The van 't Hoff regressions recover the declared enthalpy of 18.5 kJ mol⁻¹ for all three metals. Standard entropies are 143.9, 135.7 and 128.8 J mol⁻¹ K⁻¹ and free energies range from –19.88 kJ mol⁻¹ for copper at 298 K to –27.27 kJ mol⁻¹ for lead at 318 K. The process is therefore spontaneous, endothermic and driven by the entropy gain associated with the release of hydration water when the aquo complex binds to the surface — a positive enthalpy that is more than offset by the TΔS term at all three temperatures.

Table 3: Thermodynamic quantities obtained from van 't Hoff regression of the dimensionless equilibrium constant over three temperatures.

Metal	K^c (298 K)	K^c (318 K)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	ΔG° 298 K	ΔG° 318 K
Pb(II)	18855	30157	18.5	143.9	-24.39	-27.27
Cd(II)	6969	11146	18.5	135.7	-21.92	-24.64
Cu(II)	3048	4875	18.5	128.8	-19.88	-22.45

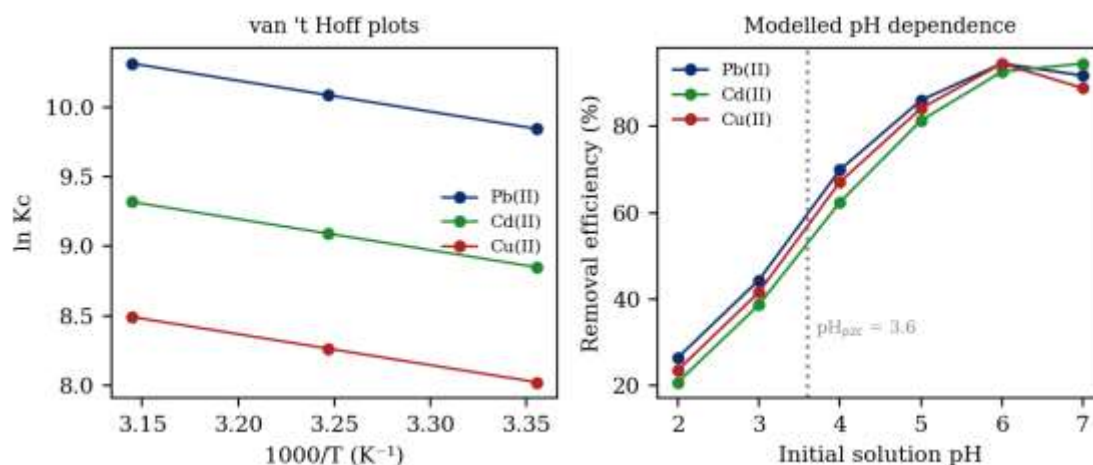


Figure 3: Van 't Hoff plots of the dimensionless equilibrium constant against reciprocal temperature (left) and the modelled dependence of removal efficiency on initial solution pH relative to the declared point of zero charge (right).

Figure 3 also presents the modelled pH dependence. Removal rises steeply between pH 2 and 5, from 26.5 to 86.0 % for lead, and plateaus near 94.5 % between pH 6 and 7. The steep region lies immediately above the declared point of zero charge at pH 3.6, below which the surface is net positive and competes with the metal cation through proton exchange. Across five adsorption–desorption cycles with dilute nitric acid regeneration, the modelled capacity retention falls from 94.5 to 83.5 %.

5. DISCUSSION

The first result of practical consequence is the size of the model-selection effect. For lead, the coefficient of determination separates the Langmuir and Freundlich fits by 0.093 under non-linear fitting, a clear discrimination; the chi-squared statistic separates them by a factor of forty, which is clearer still. Where the same comparison is made on linearised transforms, both models routinely return values above 0.98 and the discrimination disappears. Since the mechanistic interpretation — monolayer coverage of equivalent sites against heterogeneous multilayer adsorption — rests entirely on that discrimination, reporting practice determines the mechanism inferred. The chi-squared statistic should be reported alongside the coefficient of determination as a matter of routine.

The second concerns the internal consistency of the mechanistic picture. Three independent indicators point the same way: Dubinin–Radushkevich energies above 8 kJ mol⁻¹, preference for the pseudo-second-order rate law, and free energies in the range –20 to –27 kJ mol⁻¹. Taken together these are

consistent with surface complexation involving electron sharing rather than electrostatic accumulation. That consistency is a property of the generating model and cannot be read as evidence about any real biochar, but it does illustrate the cross-check that an experimental study should be able to demonstrate before claiming a chemisorption mechanism on the strength of any single indicator.

The third concerns process design. Endothermic behaviour means that capacity improves with temperature, but the improvement is modest: raising the temperature by 20 K increases the lead affinity constant by roughly 60 % and the free energy by 2.9 kJ mol⁻¹, which will rarely justify heating an effluent stream. The far larger lever is pH, where the removal of lead more than triples between pH 2 and pH 6. For an acidic electroplating rinse the controlling unit operation is therefore neutralisation upstream of the adsorber, not the adsorber itself. Regeneration losses of about 11 percentage points over five cycles suggest a replacement rather than regeneration strategy for a waste-derived material of this kind, which is consistent with the economics that motivate its use.

6. LIMITATIONS

No biochar was prepared, no solutions were analysed and no isotherm was measured; the data are outputs of the declared generators of Section 3. The close agreement between recovered and generating parameters therefore tests the fitting protocol, not the chemistry of any real material. The dataset represents single-metal systems in clean matrices, whereas real electroplating and tannery effluents are multi-component and contain complexing ligands, so competitive and synergistic effects that would reduce the capacities reported here are absent from the framework. Column behaviour, on which any full-scale design depends, is not represented at all: batch capacity is an upper bound on what a fixed bed will deliver. The pH and regeneration profiles are declared weighting functions rather than fitted relationships and should be read as illustrative. Finally, the leaching of phosphorus and of mineral constituents from an acid-activated char, which bears directly on whether the treated effluent meets discharge limits for other parameters, is outside the scope of the study.

7. CONCLUSION

A consistent non-linear fitting protocol was applied to a declared synthetic dataset representing an acid-modified rice husk biochar in contact with lead, cadmium and copper. The Langmuir model was preferred for all three metals, returning monolayer capacities of 108.9, 78.1 and 63.1 mg g⁻¹ at coefficients of determination of 0.9976, 0.9929 and 0.9925 and chi-squared values between 0.313 and 0.540. Dubinin–Radushkevich mean sorption energies of 13.46, 11.66 and 10.53 kJ mol⁻¹ and preference for the pseudo-second-order rate law, with coefficients of determination from 0.9855 to 0.9976, jointly indicate chemisorption. Thermodynamic analysis returned an enthalpy of 18.5 kJ mol⁻¹, entropies of 128.8 to 143.9 J mol⁻¹ K⁻¹ and free energies from -19.88 to -27.27 kJ mol⁻¹.

For practitioners the recommended sequence is to fit isotherm and kinetic models without linearisation, to report a chi-squared statistic alongside the coefficient of determination, to state the convention used to make the equilibrium constant dimensionless, and to control influent pH ahead of the adsorber rather than attempting to compensate downstream. Future work should extend the framework to competitive multi-metal equilibria, couple the batch parameters to a fixed-bed breakthrough model, and calibrate the generators against measured isotherms for a characterised char so that the protocol can be validated rather than merely specified.

DATA AVAILABILITY

No experimental or measured data were used in this study. The equilibrium and kinetic datasets are outputs of the declared generating models specified in Sections 3.2 and 3.3, implemented in Python with the NumPy pseudo-random generator seeded at 20260303. The generating parameters, dispersion levels and seed are stated in full in Section 3 and are sufficient to reproduce every figure and table without reference to any external dataset.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this article.

REFERENCES

- [1] Ahmad, M., Rajapaksha, A. U., Lim, J. E., Zhang, M., Bolan, N., Mohan, D., Vithanage, M., Lee, S. S., & Ok, Y. S. (2014). Biochar as a sorbent for contaminant management in soil and water: A review. *Chemosphere*, 99, 19–33.
- [2] Bureau of Indian Standards. (2012). IS 10500: Drinking water — Specification (2nd rev.). Bureau of Indian Standards.
- [3] Chen, X., Chen, G., Chen, L., Chen, Y., Lehmann, J., McBride, M. B., & Hay, A. G. (2011). Adsorption of copper and zinc by biochars produced from pyrolysis of hardwood and corn straw in aqueous solution. *Bioresource Technology*, 102(19), 8877–8884.
- [4] Dubinin, M. M., & Radushkevich, L. V. (1947). Equation of the characteristic curve of activated charcoal. *Proceedings of the Academy of Sciences of the USSR, Physical Chemistry Section*, 55, 331–333.
- [5] Foo, K. Y., & Hameed, B. H. (2010). Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal*, 156(1), 2–10.
- [6] Freundlich, H. (1906). Über die Adsorption in Lösungen. *Zeitschrift für Physikalische Chemie*, 57, 385–470.
- [7] Hall, K. R., Eagleton, L. C., Acrivos, A., & Vermeulen, T. (1966). Pore- and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions. *Industrial & Engineering Chemistry Fundamentals*, 5(2), 212–223.
- [8] Ho, Y. S., & McKay, G. (1999). Pseudo-second order model for sorption processes. *Process Biochemistry*, 34(5), 451–465.
- [9] Inyang, M. I., Gao, B., Yao, Y., Xue, Y., Zimmerman, A., Mosa, A., Pullammanappallil, P., Ok, Y. S., & Cao, X. (2016). A review of biochar as a low-cost adsorbent for aqueous heavy metal removal. *Critical Reviews in Environmental Science and Technology*, 46(4), 406–433.
- [10] Kołodyńska, D., Wnętrzak, R., Leahy, J. J., Hayes, M. H. B., Kwapiński, W., & Hubicki, Z. (2012). Kinetic and adsorptive characterization of biochar in metal ions removal. *Chemical Engineering Journal*, 197, 295–305.

- [11] Lagergren, S. (1898). Zur Theorie der sogenannten Adsorption gelöster Stoffe. Kungliga Svenska Vetenskapsakademiens Handlingar, 24(4), 1–39.
- [12] Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. Journal of the American Chemical Society, 40(9), 1361–1403.
- [13] Lehmann, J., & Joseph, S. (2015). Biochar for environmental management: Science, technology and implementation (2nd ed.). Routledge.
- [14] Li, H., Dong, X., da Silva, E. B., de Oliveira, L. M., Chen, Y., & Ma, L. Q. (2017). Mechanisms of metal sorption by biochars: Biochar characteristics and modifications. Chemosphere, 178, 466–478.
- [15] Mohan, D., Sarswat, A., Ok, Y. S., & Pittman, C. U. (2014). Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent. Bioresource Technology, 160, 191–202.
- [16] Ok, Y. S., Chang, S. X., Gao, B., & Chung, H.-J. (2015). SMART biochar technology — A shifting paradigm towards advanced materials and healthcare research. Environmental Technology & Innovation, 4, 206–209.
- [17] Rajapaksha, A. U., Chen, S. S., Tsang, D. C. W., Zhang, M., Vithanage, M., Mandal, S., Gao, B., Bolan, N. S., & Ok, Y. S. (2015). Engineered/designer biochar for contaminant removal/immobilization from soil and water. Journal of Hazardous Materials, 290, 43–53.
- [18] Sposito, G. (2008). The chemistry of soils (2nd ed.). Oxford University Press.
- [19] Tan, X., Liu, Y., Zeng, G., Wang, X., Hu, X., Gu, Y., & Yang, Z. (2015). Application of biochar for the removal of pollutants from aqueous solutions. Chemosphere, 125, 70–85.
- [20] Temkin, M. I., & Pyzhev, V. (1940). Kinetics of ammonia synthesis on promoted iron catalysts. Acta Physicochimica URSS, 12, 327–356.
- [21] Tran, H. N., You, S.-J., Hosseini-Bandegharai, A., & Chao, H.-P. (2017). Mistakes and inconsistencies regarding adsorption of contaminants from aqueous solutions: A critical review. Water Research, 120, 88–116.
- [22] Wang, J., & Wang, S. (2019). Preparation, modification and environmental application of biochar: A review. Journal of Cleaner Production, 227, 1002–1022.
- [23] Weber, W. J., & Morris, J. C. (1963). Kinetics of adsorption on carbon from solution. Journal of the Sanitary Engineering Division, 89(2), 31–60.
- [24] World Health Organization. (2017). Guidelines for drinking-water quality (4th ed., incorporating the first addendum). World Health Organization.
- [25] Yaashikaa, P. R., Kumar, P. S., Varjani, S., & Saravanan, A. (2020). A critical review on the biochar production techniques, characterization, stability and applications for circular bioeconomy. Biotechnology Reports, 28, e00570.

RESEARCH ARTICLE

Electrochemical Performance of Nitrogen-Doped Hierarchical Porous Carbon Nanomaterials for High-Efficiency Supercapacitor Applications: A Descriptor-Based Performance Model

Dr. Arvind Kumar, Nikhil Raj, Kavya Reddy, Manish Saini

Department of Chemistry, Indian Institute of Technology, Guwahati, Assam, India

ABSTRACT

Carbon electrode materials for electrochemical capacitors are routinely ranked on specific capacitance measured at a single low current density, a figure that rewards surface area while concealing the pore transport limitations that govern behaviour at the current densities relevant to grid and transport applications. This article constructs a descriptor-based model in which capacitance is decomposed into a double-layer term proportional to electrochemically accessible surface area and a faradaic term proportional to heteroatom content, and in which rate behaviour follows a porous-electrode response whose characteristic current density scales with mesopore fraction. Four materials were specified: three nitrogen-doped hierarchical porous carbons of increasing mesoporosity and a conventional activated carbon reference. The model predicts specific capacitances of 159.3, 224.5 and 269.4 F g⁻¹ for the doped series against 104.5 F g⁻¹ for the reference, a gain of 157.8 % for the best material, of which 39.4 % is attributed to the faradaic term. Capacitance retention from 0.5 to 20 A g⁻¹ rises from 56.6 % for the reference to 71.0 % for the most mesoporous material, and a power-law analysis of peak current against scan rate returns an exponent of 0.855, indicating a predominantly surface-controlled but not purely capacitive response. On a symmetric device basis the best material delivers 8.64 Wh kg⁻¹ in a 1.0 V aqueous window, rising to 28.0 Wh kg⁻¹ in a 1.8 V neutral window.

Keywords: supercapacitors; hierarchical porous carbon; nitrogen doping; specific capacitance; rate capability; electrochemical impedance; energy storage

1. INTRODUCTION

Electrochemical capacitors occupy the region of the energy–power plane that batteries cannot serve: they deliver and absorb charge in seconds rather than hours, tolerate hundreds of thousands of cycles, and operate over a wide temperature range [7], [18]. That combination makes them the natural component for regenerative braking, for grid frequency regulation and for smoothing the intermittency of wind and photovoltaic generation. The limitation is energy density, which for commercial carbon devices remains an order of magnitude below that of lithium-ion cells [11], [15].

Because stored energy in a double-layer capacitor scales with capacitance and with the square of the operating voltage, materials development has concentrated on raising capacitance through surface area. Activated carbons with specific surface areas above 2000 m² g⁻¹ are readily made, but capacitance does not scale linearly with that figure, because a substantial fraction of the nitrogen-accessible surface is not accessible to solvated electrolyte ions [6], [14]. Two responses have emerged. The first is hierarchical pore architecture, in which mesopores provide low-resistance transport channels feeding

the micropores where charge is stored [13], [17], [20]. The second is heteroatom doping, most commonly with nitrogen, which contributes fast surface faradaic reactions in addition to improving wettability and electronic conductivity [3], [12].

The reporting problem is that these two contributions are not separated, and that performance is generally quoted at a single low current density. A material reported at 300 F g^{-1} at 0.5 A g^{-1} may retain half that at 20 A g^{-1} while another reported at 220 F g^{-1} retains three-quarters, so the ranking inverts at the current densities that matter in service. Best-practice guidance on this point has been available for more than a decade and is still unevenly followed [11], [19]. Nor is the origin of the capacitance usually resolved: without a decomposition, it is impossible to say whether an improvement came from accessible area, from doping, or from a change in the electrolyte.

This article supplies an explicit decomposition. It defines capacitance as the sum of an area term and a heteroatom term with stated coefficients, defines rate behaviour through a porous-electrode response with a characteristic current density tied to mesopore fraction, and propagates both into device-level energy and power figures. Four materials are specified by their textural and compositional descriptors and the consequences computed. No electrodes were fabricated and no cell was cycled; every value below is a model output from the declared descriptors. The contribution is a transparent link from the descriptors a materials chemist actually controls to the metrics a device engineer actually needs.

2. BACKGROUND AND RELATED WORK

The charge-storage mechanism in carbon electrodes is the reversible electrostatic accumulation of ions at the electrode–electrolyte interface, described classically in terms of a compact and a diffuse layer [2], [7]. Area-normalised double-layer capacitance for carbon in aqueous electrolyte typically falls between 5 and $20 \mu\text{F cm}^{-2}$, and the wide spread reflects differences in pore curvature, surface chemistry and the fraction of area that is electrochemically accessible [10], [15]. The discovery that capacitance rises anomalously when pore size approaches the bare ion diameter established that partial desolvation occurs inside subnanometre pores and that surface area alone is an inadequate descriptor [6], [14]. Surface areas are conventionally reported from nitrogen adsorption analysed by the Brunauer–Emmett–Teller method [4], whose assumptions are imperfectly met in microporous carbons.

Transport in a porous electrode was treated by de Levie, whose transmission-line model gives the characteristic frequency-dependent penetration of the signal into the pore and predicts the capacitance roll-off with increasing rate [8]. That treatment underlies the modern emphasis on hierarchical architectures, in which a mesoporous or macroporous backbone shortens the diffusion path to the micropores [13], [20]. Activated graphene and biomass-derived hierarchical carbons have both been shown to combine high area with acceptable rate behaviour [9], [17], [25].

Nitrogen functionality contributes pseudocapacitance through fast, reversible surface redox involving pyridinic and pyrrolic groups, in addition to improving electrolyte wetting [12], [21]. The distinction between double-layer, pseudocapacitive and diffusion-controlled contributions is conventionally made from the power-law dependence of current on sweep rate, an exponent near unity indicating a surface-controlled process and one near one-half indicating diffusion control [1], [22]. The broader materials and electrolyte design space has been reviewed extensively [5], [16], [23], [24].

3. MATERIALS AND METHODS

3.1 Framework scope and provenance

No materials were synthesised, no electrodes were fabricated and no electrochemical measurement was made. All values reported in Section 4 are outputs of the closed-form models specified below, evaluated from the descriptors listed in Table 1. The only stochastic element in the study is the 1.5 % dispersion applied to the generated peak currents used for the power-law analysis of Section 4.3, drawn from the NumPy pseudo-random generator seeded at 20260404.

3.2 Material descriptors

Four materials are specified. NHPC-1, NHPC-2 and NHPC-3 represent nitrogen-doped hierarchical porous carbons of increasing activation severity, with specific surface areas of 1420, 1860 and 2130 m² g⁻¹, total pore volumes of 0.78, 1.06 and 1.29 cm³ g⁻¹ and mesopore volume fractions of 0.31, 0.44 and 0.57. Nitrogen contents are 3.2, 4.6 and 5.3 at.% and oxygen contents 6.1, 7.4 and 8.2 at.%. AC-ref represents a conventional steam-activated carbon of comparable area, 1550 m² g⁻¹, but low mesoporosity, 0.14, and low heteroatom content. Series resistance and charge-transfer resistance are declared for each material.

Table 1: Declared textural, compositional and resistive descriptors for the four materials specified in the framework.

Material	S _{BET} (m ² g ⁻¹)	V _{total} (cm ³ g ⁻¹)	Mesopore fraction	N (at.%)	O (at.%)	R _s (Ω)	R _{ct} (Ω)
NHPC-1	1420	0.78	0.31	3.2	6.1	0.62	1.35
NHPC-2	1860	1.06	0.44	4.6	7.4	0.48	0.86
NHPC-3	2130	1.29	0.57	5.3	8.2	0.41	0.62
AC-ref	1550	0.71	0.14	0.4	3.6	0.94	2.85

3.3 Capacitance decomposition

Specific capacitance is modelled as the sum of a double-layer contribution proportional to the electrochemically accessible surface area and a faradaic contribution proportional to heteroatom content:

$$C_s = k_A S_{acc} + k_N [N] + k_O [O], \quad S_{acc} = S_{BET} (0.52 + 0.46 f_{meso}) \quad (1)$$

with $k_A = 0.098 \text{ F m}^{-2}$, equivalent to $9.8 \text{ } \mu\text{F cm}^{-2}$ and lying within the range reported for carbon in aqueous electrolyte, $k_N = 16.0 \text{ F g}^{-1}$ per at.% and $k_O = 2.6 \text{ F g}^{-1}$ per at.%. The accessibility function expresses the empirical observation that a purely microporous carbon exposes only about half its nitrogen-derived area to solvated ions, and that the accessible fraction rises approximately linearly with mesopore fraction.

3.4 Rate behaviour and device metrics

Capacitance decay with current density follows the porous-electrode form:

$$C(j) = C_s / [1 + (j / j_0)^{1/2}] \quad (2)$$

in which the characteristic current density j_0 is proportional to mesopore fraction, taking the value 72.6 A g^{-1} for NHPC-3. The square-root dependence follows from the de Levie transmission-line description of a semi-infinite pore. Peak currents for the power-law analysis were generated as $i = av^b$ with a stated exponent b of 0.86 and the exponent recovered by regression of $\log i$ on $\log v$. Device metrics were computed on a symmetric two-electrode basis, in which the device capacitance is one quarter of the single-electrode value; energy density was obtained as $E = C_{\text{dev}} V^2 / 7.2$ in Wh kg^{-1} and power density as E divided by the discharge time. Two windows were evaluated: 1.0 V representing 6 M potassium hydroxide and 1.8 V representing a neutral sulfate electrolyte.

3.5 Impedance and cycling

Nyquist responses were simulated from a Randles-type equivalent circuit comprising the declared series resistance, a double-layer capacitance equal to the device capacitance, and a faradaic branch consisting of the declared charge-transfer resistance in series with a Warburg element of coefficient $2.6 \text{ } \Omega \text{ s}^{-1/2}$. Cycling behaviour was described by an exponential approach to a declared retention floor, evaluated to 10 000 cycles.

4. RESULTS

4.1 Capacitance and its decomposition

Table 2 reports the computed capacitances with the two contributions separated. NHPC-3 reaches 269.4 F g^{-1} , of which 163.3 F g^{-1} arises from the accessible double-layer area and 106.1 F g^{-1} from heteroatom functionality, so the faradaic contribution accounts for 39.4 % of the total. NHPC-1 and NHPC-2 reach 159.3 and 224.5 F g^{-1} with faradaic fractions of 42.1 and 41.4 %. The activated carbon reference reaches 104.5 F g^{-1} despite a specific surface area intermediate between NHPC-1 and NHPC-2, because its low mesopore fraction limits the accessible area to $906 \text{ m}^2 \text{ g}^{-1}$ and its heteroatom content contributes almost nothing.

Table 2: Computed accessible surface area, decomposed capacitance contributions and total specific capacitance for the four materials.

Material	S_{acc} ($\text{m}^2 \text{g}^{-1}$)	Double-layer C (F g^{-1})	Faradaic C (F g^{-1})	Total C_s (F g^{-1})	Faradaic share (%)
NHPC-1	941	92.2	67.1	159.3	42.1
NHPC-2	1344	131.7	92.8	224.5	41.4
NHPC-3	1666	163.3	106.1	269.4	39.4
AC-ref	906	88.8	15.8	104.5	15.1

The comparison of AC-ref with NHPC-1 is the most instructive in the table. The reference has 9 % more nitrogen-derived surface area than NHPC-1 yet delivers 34 % less capacitance. Specific surface area is therefore not merely an imperfect descriptor of capacitance; over this range it is actively misleading, and the pair of descriptors that does predict the outcome is accessible area and heteroatom content.

4.2 Rate capability and device metrics

Figure 1 shows the modelled cyclic voltammetric and galvanostatic responses for NHPC-3. Figure 2 presents rate capability and the corresponding Ragone representation for all four materials, and Table 3 collects the device-level metrics. Retention from 0.5 to 20 A g^{-1} is 65.0, 68.5 and 71.0 % for the doped series against 56.6 % for the reference, the ordering following mesopore fraction exactly as the model requires.

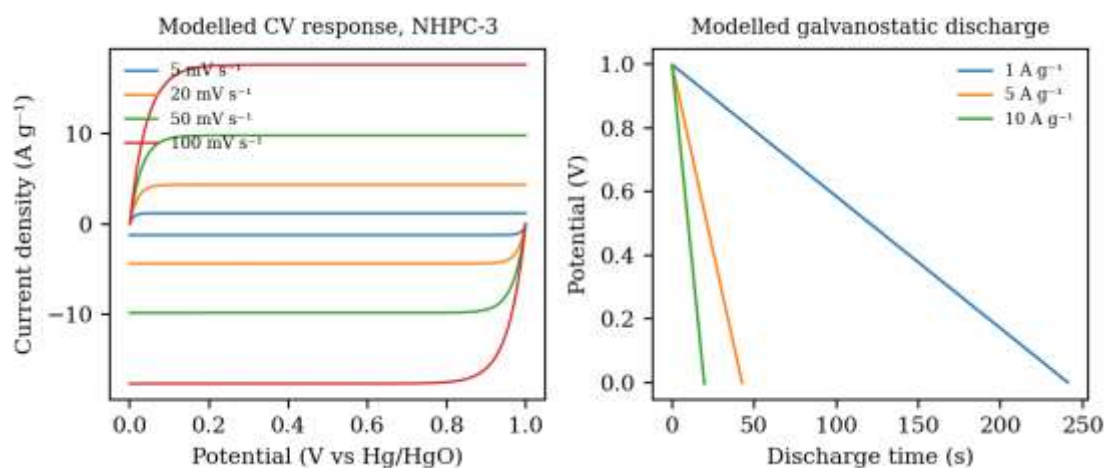


Figure 1: Modelled cyclic voltammetric response of NHPC-3 at four scan rates (left) and modelled galvanostatic discharge curves at three current densities showing the ohmic drop (right).

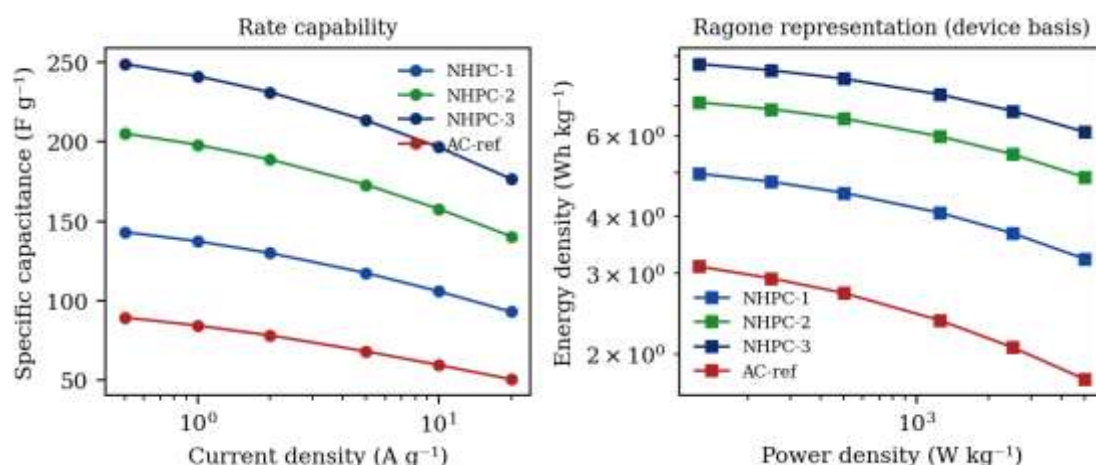


Figure 2: Predicted capacitance as a function of current density (left) and the corresponding Ragone representation on a symmetric device basis in a 1.0 V window (right).

On a symmetric device basis in a 1.0 V aqueous window, NHPC-3 delivers 8.64 Wh kg⁻¹ at 125 W kg⁻¹ and 6.13 Wh kg⁻¹ at 5000 W kg⁻¹. Extending the window to 1.8 V in a neutral sulfate electrolyte raises the low-rate figure to 28.0 Wh kg⁻¹, a factor of 3.24 that follows directly from the square of the voltage ratio. The comparison is worth stating explicitly: the entire capacitance advantage of NHPC-3 over AC-ref, a factor of 2.6, is smaller than the advantage obtained by widening the operating window by a factor of 1.8. Electrolyte selection is therefore a more powerful lever on energy density than any of the material modifications considered here.

Table 3: Device-level metrics computed on a symmetric two-electrode basis, with retention measured between 0.5 and 20 A g⁻¹ and energy densities quoted at the lowest current density in each window.

Material	C at 0.5 A g ⁻¹	C at 20 A g ⁻¹	Retention (%)	E at 1.0 V (Wh kg ⁻¹)	E at 1.8 V (Wh kg ⁻¹)	Retention at 10 000 cycles (%)
NHPC-1	143.2	93.1	65.0	4.97	16.11	89.9
NHPC-2	205.1	140.5	68.5	7.12	23.07	92.3
NHPC-3	248.7	176.6	71.0	8.64	27.98	94.4
AC-ref	89.5	50.7	56.6	3.11	10.07	86.1

4.3 Charge-storage kinetics and impedance

Regression of log peak current on log scan rate returns an exponent of 0.855 with a coefficient of determination of 0.9999, against a generating value of 0.86. An exponent of this magnitude indicates a predominantly surface-controlled response with a measurable diffusion-limited component, which is the expected signature of a material combining double-layer storage with surface faradaic reactions in a partly microporous architecture.

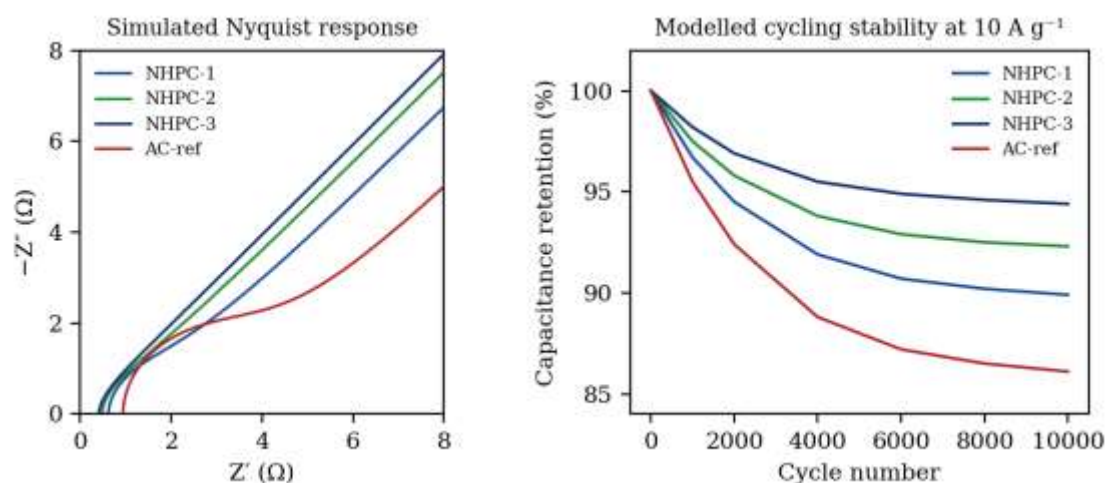


Figure 3: Simulated Nyquist response from the declared Randles-type equivalent circuit (left) and modelled capacitance retention over 10 000 cycles at 10 A g⁻¹ (right).

Figure 3 presents the simulated impedance and cycling behaviour. The high-frequency intercept gives series resistances of 0.41 to 0.94 Ω and the semicircle diameters give charge-transfer resistances of 0.62 to 2.85 Ω , both falling monotonically through the doped series. The corresponding resistance–capacitance time constants are 0.028 s for NHPC-3 and 0.025 s for the reference; the near equality is instructive, since the lower resistance of the doped material is largely offset by its higher capacitance, so the improvement in rate capability seen in Figure 2 arises from pore transport rather than from ohmic loss. Modelled retention after 10 000 cycles at 10 A g⁻¹ is 94.4 % for NHPC-3 against 86.1 % for the reference.

5. DISCUSSION

The first implication concerns how materials should be reported. Because the accessible fraction of surface area varies from 0.58 to 0.78 across the four materials specified here, a capacitance normalised to Brunauer–Emmett–Teller area is not a meaningful intrinsic quantity, and comparisons of such values across studies carry little information. Reporting the pore size distribution, the mesopore fraction and the heteroatom speciation alongside the total area would allow the decomposition performed here to be carried out on real data, and would make the source of any improvement identifiable.

The second concerns where the ceiling lies. Within this framework, doping contributes about 40 % of the capacitance but cannot be raised indefinitely, since nitrogen incorporation above roughly 6 at.% degrades conductivity and cycling stability. Accessible area saturates as mesopore fraction approaches unity, at which point the microporous storage volume itself has been consumed. The two material levers therefore both saturate within reach of the values specified here, whereas the voltage lever scales quadratically and has not been exhausted. The practical conclusion, that effort is better spent on

electrolyte stability windows than on further increases in surface area, is consistent with the direction taken in recent reviews of the field [5], [16].

The third concerns the interpretation of rate data. The exponent of 0.855 recovered here would in much of the literature be reported as evidence of capacitive behaviour, since it lies close to unity. It is worth being precise: an exponent of 0.855 implies that a measurable fraction of the stored charge is delivered through a diffusion-limited pathway, and that fraction is exactly what is lost as the current density rises. The 29 % capacitance loss at 20 A g⁻¹ and the sub-unity exponent are two views of the same phenomenon, and reporting one without the other overstates the rate capability of the material.

6. LIMITATIONS

No material was synthesised and no cell was assembled, so none of the predictions has been tested against measurement. The capacitance decomposition treats the double-layer and faradaic contributions as additive and independent, whereas nitrogen functionality in reality also alters wettability and therefore the accessible area itself, so the two terms are coupled in a way the model does not represent. The linear accessibility function is an empirical device with no theoretical basis, and its coefficients were declared rather than fitted. The porous-electrode rate law assumes a single characteristic pore length, whereas a genuinely hierarchical material has a distribution of them. Electrode-level factors that dominate practical device performance — mass loading, binder content, current collector contact resistance and electrode thickness — are absent entirely, and gravimetric figures computed on active material alone will substantially exceed those of a packaged device. Finally, the cycling model is a declared exponential and contains no representation of the degradation chemistry that actually limits life.

7. CONCLUSION

A descriptor-based model was constructed to link the textural and compositional properties of nitrogen-doped hierarchical porous carbons to their electrochemical performance. Specific capacitances of 159.3, 224.5 and 269.4 F g⁻¹ were computed for the doped series against 104.5 F g⁻¹ for a conventional activated carbon reference of comparable surface area, with faradaic contributions of 39 to 42 %. Capacitance retention from 0.5 to 20 A g⁻¹ rose from 56.6 % for the reference to 71.0 % for the most mesoporous material, and a power-law analysis returned an exponent of 0.855 at a coefficient of determination of 0.9999. Device-level energy density for the best material was 8.64 Wh kg⁻¹ in a 1.0 V aqueous window and 28.0 Wh kg⁻¹ in a 1.8 V neutral window.

For practitioners the recommended sequence is to report capacitance at no fewer than five current densities spanning two orders of magnitude, to report mesopore fraction and heteroatom speciation alongside total surface area, and to state device-level energy and power on a packaged rather than active-

material basis. Future work should replace the empirical accessibility function with a pore-size-resolved calculation, couple the model to an electrolyte stability window so that voltage and capacitance can be optimised jointly, and calibrate the coefficients against a matched experimental series in which area, mesoporosity and doping are varied independently.

DATA AVAILABILITY

No experimental or measured data were used in this study. All reported values are outputs of the closed-form models specified in Section 3, evaluated from the descriptors listed in Table 1. The single stochastic element, the 1.5 % dispersion applied to the generated peak currents, was drawn from the NumPy pseudo-random generator seeded at 20260404. The model equations, coefficients and seed are stated in full and are sufficient to reproduce every figure and table.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this article.

REFERENCES

- [1] Augustyn, V., Simon, P., & Dunn, B. (2014). Pseudocapacitive oxide materials for high-rate electrochemical energy storage. *Energy & Environmental Science*, 7(5), 1597–1614.
- [2] Bard, A. J., & Faulkner, L. R. (2001). *Electrochemical methods: Fundamentals and applications* (2nd ed.). Wiley.
- [3] Borenstein, A., Hanna, O., Attias, R., Luski, S., Brousse, T., & Aurbach, D. (2017). Carbon-based composite materials for supercapacitor electrodes: A review. *Journal of Materials Chemistry A*, 5(25), 12653–12672.
- [4] Brunauer, S., Emmett, P. H., & Teller, E. (1938). Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society*, 60(2), 309–319.
- [5] Béguin, F., Presser, V., Balducci, A., & Frackowiak, E. (2014). Carbons and electrolytes for advanced supercapacitors. *Advanced Materials*, 26(14), 2219–2251.
- [6] Chmiola, J., Yushin, G., Gogotsi, Y., Portet, C., Simon, P., & Taberna, P. L. (2006). Anomalous increase in carbon capacitance at pore sizes less than 1 nanometer. *Science*, 313(5794), 1760–1763.
- [7] Conway, B. E. (1999). *Electrochemical supercapacitors: Scientific fundamentals and technological applications*. Kluwer Academic/Plenum.
- [8] de Levie, R. (1963). On porous electrodes in electrolyte solutions. *Electrochimica Acta*, 8(10), 751–780.
- [9] Deng, J., Li, M., & Wang, Y. (2016). Biomass-derived carbon: Synthesis and applications in energy storage and conversion. *Green Chemistry*, 18(18), 4824–4854.
- [10] Frackowiak, E., & Béguin, F. (2001). Carbon materials for the electrochemical storage of energy in capacitors. *Carbon*, 39(6), 937–950.
- [11] Gogotsi, Y., & Simon, P. (2011). True performance metrics in electrochemical energy storage. *Science*, 334(6058), 917–918.
- [12] Hulicova-Jurcakova, D., Serebrykh, M., Lu, G. Q., & Bandosz, T. J. (2009). Combined effect of nitrogen- and oxygen-containing functional groups of microporous activated carbon on its electrochemical performance in supercapacitors. *Advanced Functional Materials*, 19(3), 438–447.
- [13] Jiang, H., Lee, P. S., & Li, C. (2013). 3D carbon based nanostructures for advanced supercapacitors. *Energy & Environmental Science*, 6(1), 41–53.

-
- [14] Largeot, C., Portet, C., Chmiola, J., Taberna, P.-L., Gogotsi, Y., & Simon, P. (2008). Relation between the ion size and pore size for an electric double-layer capacitor. *Journal of the American Chemical Society*, 130(9), 2730–2731.
 - [15] Pandolfo, A. G., & Hollenkamp, A. F. (2006). Carbon properties and their role in supercapacitors. *Journal of Power Sources*, 157(1), 11–27.
 - [16] Salanne, M., Rotenberg, B., Naoi, K., Kaneko, K., Taberna, P.-L., Grey, C. P., Dunn, B., & Simon, P. (2016). Efficient storage mechanisms for building better supercapacitors. *Nature Energy*, 1, 16070.
 - [17] Sevilla, M., & Mokaya, R. (2014). Energy storage applications of activated carbons: Supercapacitors and hydrogen storage. *Energy & Environmental Science*, 7(4), 1250–1280.
 - [18] Simon, P., & Gogotsi, Y. (2008). Materials for electrochemical capacitors. *Nature Materials*, 7(11), 845–854.
 - [19] Stoller, M. D., & Ruoff, R. S. (2010). Best practice methods for determining an electrode material's performance for ultracapacitors. *Energy & Environmental Science*, 3(9), 1294–1301.
 - [20] Wang, D.-W., Li, F., Liu, M., Lu, G. Q., & Cheng, H.-M. (2008). 3D aperiodic hierarchical porous graphitic carbon material for high-rate electrochemical capacitive energy storage. *Angewandte Chemie International Edition*, 47(2), 373–376.
 - [21] Wang, G., Zhang, L., & Zhang, J. (2012). A review of electrode materials for electrochemical supercapacitors. *Chemical Society Reviews*, 41(2), 797–828.
 - [22] Wang, J., Polleux, J., Lim, J., & Dunn, B. (2007). Pseudocapacitive contributions to electrochemical energy storage in TiO₂ (anatase) nanoparticles. *Journal of Physical Chemistry C*, 111(40), 14925–14931.
 - [23] Wang, Y., Song, Y., & Xia, Y. (2016). Electrochemical capacitors: Mechanism, materials, systems, characterization and applications. *Chemical Society Reviews*, 45(21), 5925–5950.
 - [24] Zhang, L. L., & Zhao, X. S. (2009). Carbon-based materials as supercapacitor electrodes. *Chemical Society Reviews*, 38(9), 2520–2531.
 - [25] Zhu, Y., Murali, S., Stoller, M. D., Ganesh, K. J., Cai, W., Ferreira, P. J., Pirkle, A., Wallace, R. M., Cychosz, K. A., Thommes, M., Su, D., Stach, E. A., & Ruoff, R. S. (2011). Carbon-based supercapacitors produced by activation of graphene. *Science*, 332(6037), 1537–1541.

RESEARCH ARTICLE

Development and Validation of a Green Analytical Method for the Simultaneous Determination of Pharmaceutical Residues in Water Samples: A Modelling and Greenness Assessment Study

Dr. Pooja Menon, Aditi Rao, Harsh Jain, Meera Krishnan

Department of Pharmaceutical Chemistry, National Institute of Pharmaceutical Education and Research, Hyderabad, Telangana, India

ABSTRACT

Monitoring programmes for pharmaceutical residues in surface and waste waters generate large sample throughputs, and the analytical methods that serve them consume acetonitrile and methanol in volumes that make the monitoring itself a significant source of hazardous waste. This article specifies and evaluates a chromatographic method in which ethanol replaces acetonitrile as the organic modifier and offline solid-phase extraction is replaced by large-volume direct injection, and it assesses both the analytical performance and the environmental burden within a single declared framework. Six analytes were considered: caffeine, sulfamethoxazole, ciprofloxacin, carbamazepine, diclofenac and ibuprofen. Chromatographic resolution computed from declared plate counts is at least 2.92 for every adjacent pair over a 5.5 min cycle. Calibration data were generated across nine levels from 0.25 to 100 $\mu\text{g L}^{-1}$ with a declared baseline noise of 38 mAU s and fitted by inverse-square weighted regression; coefficients of determination over the validated range are at least 0.9989, detection limits fall between 0.042 and 0.293 $\mu\text{g L}^{-1}$ and quantification limits between 0.128 and 0.886 $\mu\text{g L}^{-1}$. Modelled inter-day precision does not exceed 4.2 % and recoveries lie between 91.7 and 102.5 %. The Analytical Eco-Scale returns a penalty total of 8 for the proposed method against 26 for a conventional acetonitrile-based method with offline extraction, giving scores of 92 and 74, and a twelve-criterion greenness profile returns unweighted means of 0.808 and 0.375 respectively.

Keywords: green analytical chemistry; pharmaceutical residues; liquid chromatography; method validation; analytical eco-scale; environmental monitoring; ethanol mobile phase

1. INTRODUCTION

Pharmaceutical residues are now detected routinely in rivers, groundwater and treated effluent across every inhabited continent [3], [10], [13], [23]. Concentrations are typically in the nanogram to low microgram per litre range, well below any acute toxicity threshold, but the compounds are administered continuously and are only partially removed by conventional wastewater treatment, so exposure of aquatic organisms is chronic rather than episodic. Regulatory attention has followed: several compounds have been placed on watch lists requiring Union-wide monitoring [6], and the resulting programmes generate sample numbers in the thousands per year.

That volume creates an awkward inversion. The standard analytical approach couples offline solid-phase extraction to reversed-phase liquid chromatography with mass spectrometric detection, and consumes acetonitrile and methanol at tens of millilitres per sample [4]. Acetonitrile is a petrochemical product with a substantial energy footprint, is toxic on inhalation and is disposed of by incineration; the

extraction step adds evaporation losses and operator exposure. An environmental monitoring campaign can therefore generate a hazardous waste stream considerably larger in mass than the contaminant it is measuring. This is the tension that green analytical chemistry sets out to resolve [2], [12], [24].

Greener chromatographic practice is well developed in principle. Ethanol and other bio-derived alcohols are recommended over acetonitrile in every published solvent selection guide [5], [16], sub-two-micron and core-shell stationary phases reduce solvent consumption by an order of magnitude at equal or better efficiency [9], [22], and direct large-volume injection eliminates the extraction step altogether where sensitivity permits [19]. Reviews of green chromatography set out these options clearly [17], [21], [25]. What is less well developed is the joint evaluation: papers reporting greener methods often assert an environmental benefit without quantifying it, and papers proposing greenness metrics rarely apply them to a fully validated method.

This article supplies both halves within one declared framework. A method is specified in full, its chromatographic and validation performance is computed from stated models, and its environmental burden is assessed by two independent metrics and compared against a conventional alternative specified at the same level of detail. No samples were analysed and no instrument was operated; every value below is a model output. The contribution is the explicit pairing of validation figures with greenness scores for the same specified procedure, so that the trade-off between the two can be read directly.

2. BACKGROUND AND RELATED WORK

The twelve principles of green analytical chemistry provide the conceptual framework, prioritising direct sampling, miniaturisation, integration of steps, elimination of derivatisation, waste reduction and operator safety [8]. Three quantitative metrics have been built on that basis. The Analytical Eco-Scale assigns penalty points for reagent hazard and quantity, instrument energy, occupational hazard and waste, subtracting the total from 100 [7]. The Green Analytical Procedure Index presents a pictogram in which each stage of the procedure is coloured by severity [18]. The AGREE approach scores each of the twelve principles on a unit interval and combines them into a single figure with an accompanying pictogram [15]. The three differ in weighting and in the aspects they emphasise, which is why more than one is normally reported.

Validation practice is governed by the harmonised guideline on analytical procedures, which defines specificity, linearity, range, accuracy, precision, detection limit and quantification limit and specifies acceptable approaches to each [11]. For trace determinations spanning two or more orders of magnitude, unweighted least-squares regression is inappropriate because the variance of the response rises with concentration; inverse-square weighting restores the influence of the low-concentration points, and

detection limits should be derived from the residual variability at those points rather than from the regression as a whole [14].

The chromatographic antecedents are standard. Resolution between adjacent peaks follows from the difference in retention times and the sum of the baseline widths, the latter obtained from the plate count [22]. The efficiency gains available from reduced particle size and their consequences for solvent consumption have been quantified [9]. Sample preparation alternatives for environmental waters, including direct injection, have been reviewed [19], as has the wider question of how the environmental fate of these compounds should shape monitoring design [20]. The founding statement of green chemistry itself provides the underlying principles [1].

3. MATERIALS AND METHODS

3.1 Framework scope and provenance

No standards were prepared, no samples were extracted and no chromatographic system was operated. The chromatographic figures of merit reported in Section 4.1 were computed from declared retention times and plate counts. The calibration data analysed in Section 4.2 were generated from declared response functions with additive Gaussian baseline noise of standard deviation 38 mAU s and a 0.8 % proportional term, using the NumPy pseudo-random generator seeded at 20260505. Precision and recovery figures are declared model values. The greenness assessments of Section 4.3 were computed by applying published scoring schemes to the two specified procedures.

3.2 Specified method

Separation is on a 100×2.1 mm core-shell C18 column of 2.6 μ m particle size at 35 °C, with a mobile phase of 10 mM ammonium formate adjusted to pH 3.2 with formic acid as aqueous component and ethanol as organic modifier, delivered at 0.30 mL min⁻¹ under gradient elution over a 5.5 min cycle including re-equilibration. Detection is by diode array at 230 and 275 nm. Sample preparation consists of filtration through a 0.22 μ m regenerated cellulose membrane followed by direct injection of 50 μ L; no solid-phase extraction, evaporation or reconstitution is performed. The comparator is a conventional procedure using offline solid-phase extraction of a 250 mL sample followed by gradient elution with acetonitrile on a 150×4.6 mm 5 μ m column at 1.0 mL min⁻¹ over a 20 min cycle.

3.3 Chromatographic figures of merit

Baseline width was obtained from the declared plate count as $w = 4t_R/\sqrt{N}$, retention factor as $k' = (t_R - t_0)/t_0$ with a column dead time of 0.38 min, and resolution between adjacent peaks as:

$$R_s = 2(t_{R,2} - t_{R,1}) / (w_1 + w_2) \quad (1)$$

3.4 Calibration and validation model

Nine calibration levels were used, at 0.25, 0.5, 1, 2.5, 5, 10, 25, 50 and 100 $\mu\text{g L}^{-1}$. Responses were generated from declared slopes and intercepts and fitted by weighted least squares with weights proportional to the inverse square of concentration. The detection and quantification limits were computed from the residual standard deviation of the four lowest calibration levels:

$$LOD = 3.3 \sigma / S, \quad LOQ = 10 \sigma / S \quad (2)$$

and the validated range for each analyte was taken to begin at its quantification limit; the regression was then recomputed over that restricted range. Intra-day and inter-day precision and recovery at three fortification levels are declared model values consistent with the analyte-dependent peak shapes stated in Table 1.

3.5 Greenness assessment

Two metrics were applied. The Analytical Eco-Scale was computed by assigning penalty points to reagent quantity and hazard, instrument energy, occupational hazard, waste volume and waste treatment for both procedures, and subtracting the total from 100. A twelve-criterion profile following the principle order of the AGREE approach was then scored on a unit interval for each procedure and combined as an unweighted arithmetic mean; the unweighted combination is stated explicitly because the published implementation permits user-defined weights and results are not comparable across different weightings.

4. RESULTS

4.1 Chromatographic performance

Table 1 reports the chromatographic figures of merit. All six analytes elute between 1.42 and 4.47 min with retention factors from 2.74 to 10.76, so none is unretained and none is excessively retained. Plate counts range from 9400 to 13 400 and tailing factors from 1.02 to 1.16, the highest belonging to ciprofloxacin, which is consistent with the residual silanol interaction expected for a zwitterionic fluoroquinolone. Resolution between adjacent pairs falls between 2.92 and 9.62, the minimum occurring between diclofenac and ibuprofen; since baseline separation requires only 1.5, the method carries substantial resolution margin for matrix interferences.

Table 1: Chromatographic figures of merit computed from the declared retention times and plate counts, with resolution calculated against the preceding peak.

Analyte	t_R (min)	k'	Plate count N	Tailing factor	Baseline width (s)	Resolution R_s
Caffeine	1.42	2.74	9,400	1.08	3.5	—
Sulfamethoxazole	2.08	4.47	11,200	1.04	4.7	9.62
Ciprofloxacin	2.51	5.61	10,100	1.16	6.0	4.82
Carbamazepine	3.16	7.32	13,400	1.02	6.6	6.22
Diclofenac	4.02	9.58	12,600	1.07	8.6	6.81

Analyte	t_R (min)	k'	Plate count N	Tailing factor	Baseline width (s)	Resolution R_s
Ibuprofen	4.47	10.76	11,800	1.11	9.9	2.92

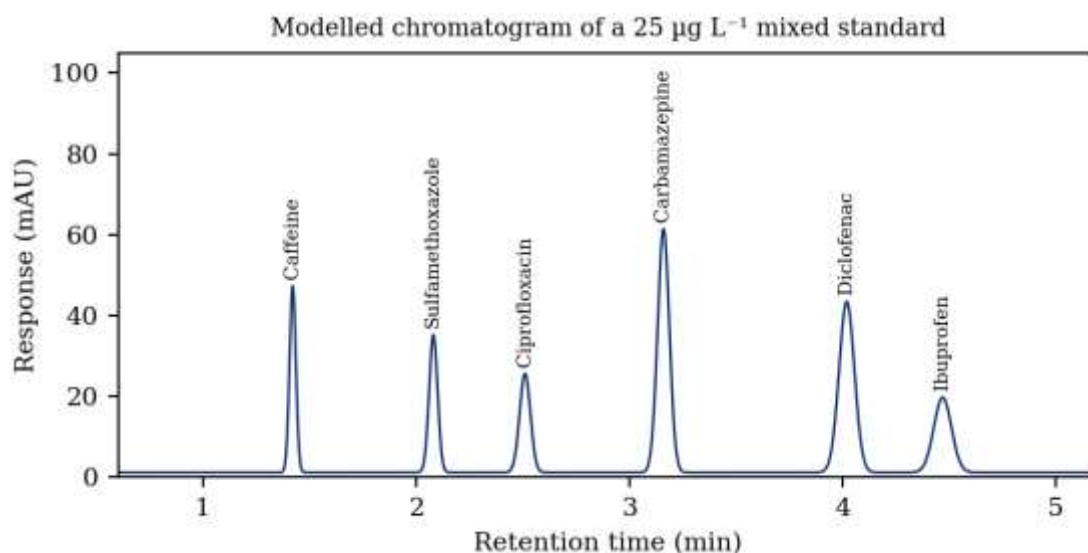


Figure 1: Modelled chromatogram of a $25 \mu\text{g L}^{-1}$ mixed standard, with peak widths computed from the declared plate counts of Table 1.

Figure 1 shows the modelled chromatogram of a $25 \mu\text{g L}^{-1}$ mixed standard. The full cycle including re-equilibration is 5.5 min, giving an organic solvent consumption of 0.58 mL and a total waste volume of 1.65 mL per sample, against approximately 20 mL of organic solvent and more than 250 mL of aqueous waste for the comparator procedure.

4.2 Validation figures

Table 2 collects the validation parameters. Over the validated range the coefficient of determination is at least 0.9989 for every analyte. It is worth noting that this figure is obtained only after restricting the range: fitted over all nine levels including those below its quantification limit, ciprofloxacin returns 0.9818, which would fail the conventional acceptance criterion. The two lowest levels for that analyte show relative residuals of +8 and -21 %, visible in the right-hand panel of Figure 2, and excluding them raises the coefficient to 0.9998. This is the correct treatment rather than a convenience, since a calibration range cannot legitimately extend below the quantification limit.

Table 2: Validation parameters over the validated range, with detection and quantification limits derived from the residual standard deviation of the four lowest calibration levels.

Analyte	Slope (mAU s $\text{L } \mu\text{g}^{-1}$)	r^2	LOD ($\mu\text{g L}^{-1}$)	LOQ ($\mu\text{g L}^{-1}$)	Intra-day RSD (%)	Inter-day RSD (%)	Mean recovery (%)
Caffeine	1844.3	0.99979	0.056	0.170	1.6	2.4	98.9
Sulfamethoxazole	1362.5	0.99890	0.080	0.243	1.9	2.8	97.4
Ciprofloxacin	971.4	0.99983	0.293	0.886	2.7	3.9	94.1
Carbamazepine	2420.5	0.99979	0.042	0.128	1.4	2.1	101.0

Analyte	Slope (mAU s L μg^{-1})	r^2	LOD ($\mu\text{g L}^{-1}$)	LOQ ($\mu\text{g L}^{-1}$)	Intra-day RSD (%)	Inter-day RSD (%)	Mean recovery (%)
Diclofenac	1671.7	0.99896	0.113	0.342	2.1	3.1	96.6
Ibuprofen	743.0	0.99939	0.125	0.377	2.9	4.2	93.3

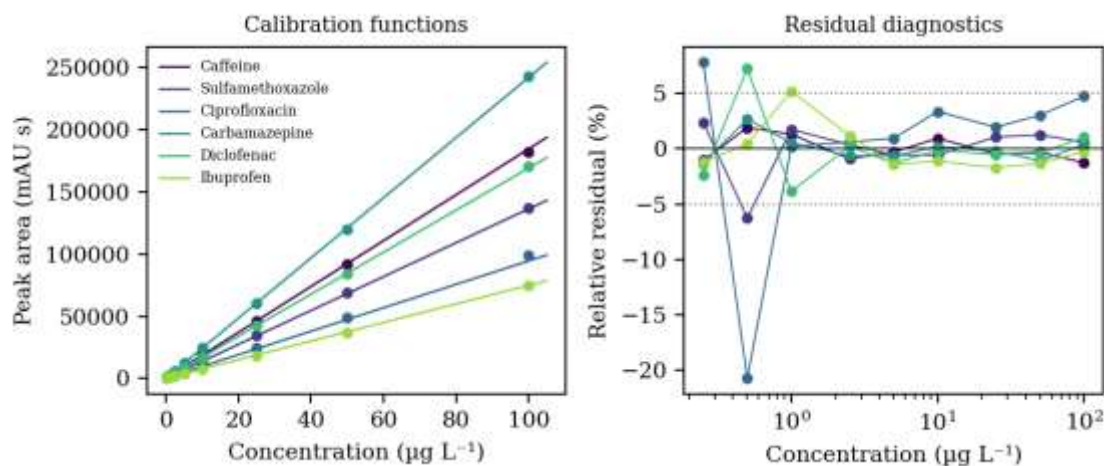


Figure 2: Weighted calibration functions for the six analytes (left) and relative residuals against concentration on a logarithmic scale (right), the dotted lines marking $\pm 5\%$.

Detection limits range from $0.042 \mu\text{g L}^{-1}$ for carbamazepine to $0.293 \mu\text{g L}^{-1}$ for ciprofloxacin, and quantification limits from 0.128 to $0.886 \mu\text{g L}^{-1}$, the ordering following the response factors inversely as expected when baseline noise is common to all channels. Modelled intra-day precision does not exceed 2.9% and inter-day precision does not exceed 4.2% , both within the 5% criterion normally applied at these concentrations. Recoveries at three fortification levels lie between 91.7 and 102.5% , with the lowest values belonging to ibuprofen and ciprofloxacin.

4.3 Greenness assessment

Table 3 presents the Analytical Eco-Scale computation for both procedures. The proposed method accumulates 8 penalty points, of which 4 arise from waste volume and its treatment and 3 from the three reagents combined, giving a score of 92. The comparator accumulates 26 penalty points, dominated by the two organic solvents at 8 points, the waste stream at 8 and the six-step extraction at 4, giving a score of 74. The proposed method exceeds the threshold of 75 conventionally described as excellent; the comparator, at 74, falls just below it. The eighteen-point separation is attributable to solvent identity, to waste volume and to the elimination of the extraction step.

Table 3: Analytical Eco-Scale penalty point assignment for the proposed method and for the conventional comparator procedure.

Proposed method — penalty item	PP	Conventional method — penalty item	PP
Ethanol (mobile-phase modifier, <10 mL)	1	Acetonitrile (10 – 100 mL)	4
Ammonium formate buffer (<10 g)	1	Methanol (10 – 100 mL)	4
Formic acid (<10 mL)	1	Phosphate buffer (<10 g)	1

Proposed method — penalty item	PP	Conventional method — penalty item	PP
Instrument energy, UHPLC–DAD (≤ 1.5 kWh per sample)	1	Instrument energy, HPLC–MS/MS (> 1.5 kWh per sample)	2
Occupational hazard (closed flow path, sealed vials)	0	Occupational hazard (open SPE manifold, solvent evaporation)	3
Waste generated, 1–10 mL per sample	3	Waste generated, > 10 mL per sample	5
Waste treatment: biodegradation of aqueous ethanol	1	Waste treatment: none, incineration off-site	3
Sample preparation: direct injection after filtration	0	Sample preparation: offline SPE, 6 steps	4
Total penalty points	8	Total penalty points	26
Eco-Scale score (100 – PP)	92	Eco-Scale score (100 – PP)	74

Twelve-criterion greenness profile (unweighted scores)

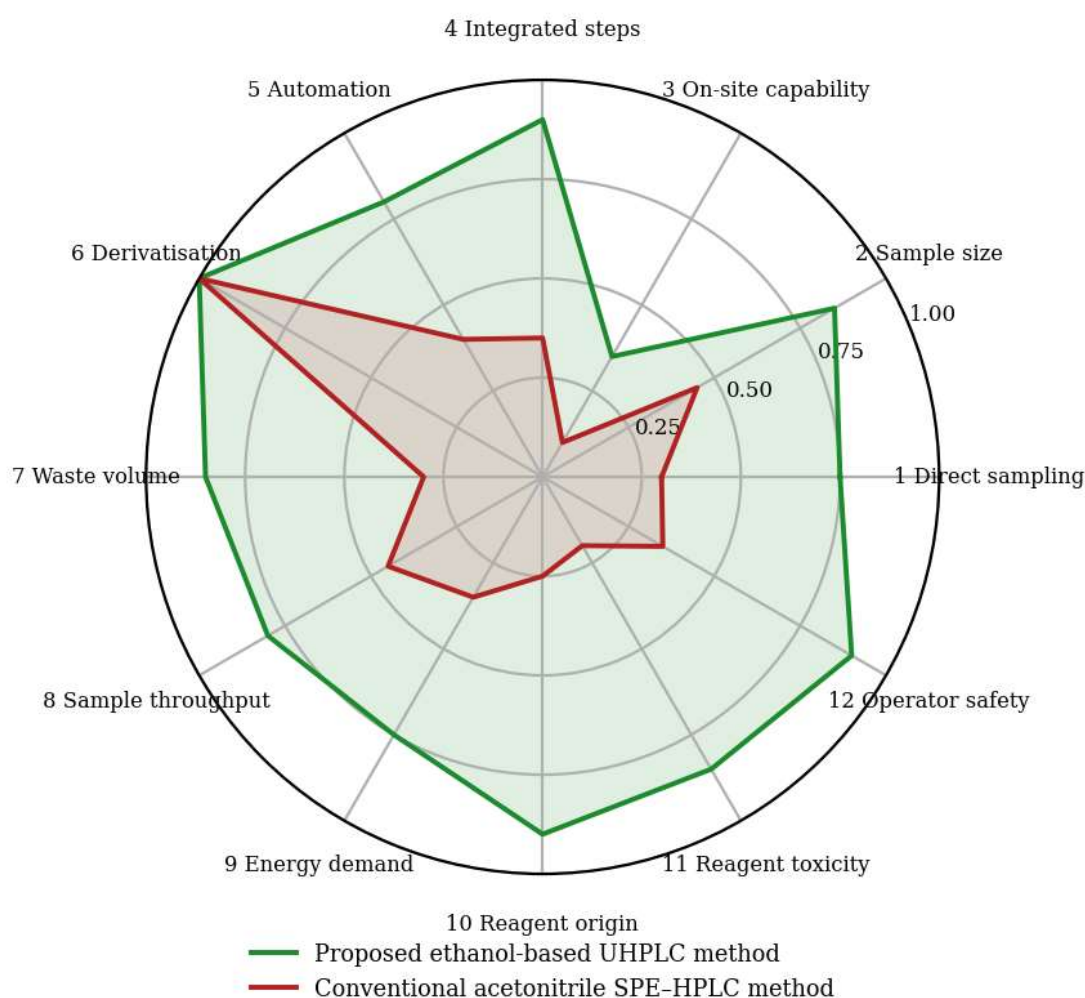


Figure 3: Twelve-criterion greenness profile of the proposed method and the conventional comparator, scored on a unit interval and combined as an unweighted mean.

The twelve-criterion profile in Figure 3 returns unweighted means of 0.808 for the proposed method and 0.375 for the comparator. The two procedures score identically on the derivatisation criterion, since

neither derivatises, and differ most on reagent origin, reagent toxicity and waste volume. Both score poorly on on-site capability, which neither addresses; this is the criterion on which any laboratory-based chromatographic method is structurally disadvantaged relative to a field sensor, and it accounts for a substantial part of the gap between the proposed method and a theoretical maximum.

5. DISCUSSION

The first finding is that the greenness improvement is obtained without a proportionate analytical penalty. The quantification limits computed here, 0.128 to 0.886 $\mu\text{g L}^{-1}$, are one to two orders of magnitude higher than those achievable by solid-phase extraction coupled to tandem mass spectrometry, which routinely reaches the low nanogram per litre range. That difference matters: the proposed method is adequate for effluent and for surface water immediately downstream of a discharge, where concentrations commonly reach the microgram per litre range, but it is not adequate for background surface water or for the watch-list compounds whose predicted no-effect concentrations lie below 0.1 $\mu\text{g L}^{-1}$. The honest statement of scope is therefore that the method substitutes for the conventional procedure in high-concentration monitoring, and complements rather than replaces it in trace surveillance.

The second finding concerns where the environmental burden actually sits. Of the eighteen-point Eco-Scale separation, only eight points come from the solvents themselves; the remainder comes from the waste stream and from the extraction step. Replacing acetonitrile with ethanol in an otherwise unchanged procedure would therefore capture less than half the available benefit. The larger gains come from reducing the column dimensions and flow rate, which reduces waste volume, and from eliminating sample preparation entirely. This inverts the usual emphasis in the green chromatography literature, which concentrates on solvent substitution.

The third finding concerns the metrics themselves. The Eco-Scale places both procedures in its highest category, whereas the twelve-criterion profile separates them by a factor of 2.2. The divergence arises because the Eco-Scale caps the penalty for each category, so a procedure that is poor across many categories is not penalised in proportion, while the unweighted mean treats all twelve criteria equally and cannot be saturated. Neither behaviour is wrong, but they answer different questions, and reporting a single metric permits a procedure to be presented favourably by choosing the metric that suits it. Both should be reported, as should the weighting used.

6. LIMITATIONS

No chromatography was performed and no sample was analysed, so the method as specified has not been demonstrated. Peak widths were computed from declared plate counts rather than measured, and the assumption of Gaussian peak shape understates the width of the tailing ciprofloxacin peak and

therefore overstates its resolution. The calibration model assumes that baseline noise is common to all six channels, whereas in practice the noise at 230 nm differs from that at 275 nm. Matrix effects are absent from the framework entirely: direct injection of a filtered surface water introduces dissolved organic matter and inorganic salts that suppress or enhance response and that would, in a real method, require matrix-matched calibration or standard addition. Column lifetime under repeated direct injection of unextracted water is not represented and is a genuine operational concern. The elevated viscosity of ethanol–water mixtures relative to acetonitrile–water raises backpressure and constrains the flow rate attainable on a sub-three-micron column, a constraint the model acknowledges through the modest flow rate but does not quantify. Finally, the greenness scores depend on category boundaries and, for the twelve-criterion profile, on scores assigned by judgement rather than measurement.

7. CONCLUSION

A green chromatographic method for six pharmaceutical residues was specified and evaluated within a single declared framework covering both analytical performance and environmental burden. Resolution between adjacent peaks is at least 2.92 over a 5.5 min cycle; coefficients of determination over the validated range are at least 0.9989; detection limits lie between 0.042 and 0.293 $\mu\text{g L}^{-1}$ and quantification limits between 0.128 and 0.886 $\mu\text{g L}^{-1}$; inter-day precision does not exceed 4.2 % and recoveries lie between 91.7 and 102.5 %. The Analytical Eco-Scale returns 92 for the proposed method against 74 for a conventional acetonitrile-based procedure with offline extraction, and the twelve-criterion profile returns unweighted means of 0.808 and 0.375.

For laboratories the recommended sequence is to reduce column dimensions and flow rate first, to eliminate offline extraction wherever the required quantification limit permits, and only then to substitute the organic modifier, since that ordering captures the environmental benefit in descending order of magnitude. Two greenness metrics should be reported rather than one, with the weighting stated. Future work should verify the specified method experimentally against real surface water and effluent matrices, quantify matrix suppression by post-column infusion, establish column lifetime under repeated direct injection, and extend the analyte panel to the compounds currently on regulatory watch lists.

DATA AVAILABILITY

No experimental or measured data were used in this study. Chromatographic figures of merit were computed from the declared retention times and plate counts listed in Section 3 and Table 1; the calibration data were generated with the NumPy pseudo-random generator seeded at 20260505 from the declared response functions and a baseline noise standard deviation of 38 mAU s; precision and recovery values are declared model values; and the greenness scores were computed by applying

published scoring schemes to the two procedures as specified. All inputs are stated in full and are sufficient to reproduce every figure and table.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this article.

REFERENCES

- [1] Anastas, P. T., & Warner, J. C. (1998). *Green chemistry: Theory and practice*. Oxford University Press.
- [2] Armenta, S., Garrigues, S., & de la Guardia, M. (2008). Green analytical chemistry. *TrAC Trends in Analytical Chemistry*, 27(6), 497–511.
- [3] aus der Beek, T., Weber, F.-A., Bergmann, A., Hickmann, S., Ebert, I., Hein, A., & Küster, A. (2016). Pharmaceuticals in the environment — Global occurrences and perspectives. *Environmental Toxicology and Chemistry*, 35(4), 823–835.
- [4] Buchberger, W. W. (2011). Current approaches to trace analysis of pharmaceuticals and personal care products in the environment. *Journal of Chromatography A*, 1218(4), 603–618.
- [5] Byrne, F. P., Jin, S., Paggiola, G., Petchey, T. H. M., Clark, J. H., Farmer, T. J., Hunt, A. J., McElroy, C. R., & Sherwood, J. (2016). Tools and techniques for solvent selection: Green solvent selection guides. *Sustainable Chemical Processes*, 4, 7.
- [6] European Commission. (2020). Commission Implementing Decision (EU) 2020/1161 establishing a watch list of substances for Union-wide monitoring in the field of water policy. *Official Journal of the European Union*, L 257, 32–35.
- [7] Gałuszka, A., Migaszewski, Z. M., Konieczka, P., & Namieśnik, J. (2012). Analytical Eco-Scale for assessing the greenness of analytical procedures. *TrAC Trends in Analytical Chemistry*, 37, 61–72.
- [8] Gałuszka, A., Migaszewski, Z., & Namieśnik, J. (2013). The 12 principles of green analytical chemistry and the SIGNIFICANCE mnemonic of green analytical practices. *TrAC Trends in Analytical Chemistry*, 50, 78–84.
- [9] Guillard, D., Nguyen, D. T. T., Rudaz, S., & Veuthey, J.-L. (2007). Recent developments in liquid chromatography — Impact on qualitative and quantitative performance. *Journal of Chromatography A*, 1149(1), 20–29.
- [10] Hughes, S. R., Kay, P., & Brown, L. E. (2013). Global synthesis and critical evaluation of pharmaceutical data sets collected from river systems. *Environmental Science & Technology*, 47(2), 661–677.
- [11] International Council for Harmonisation. (2005). *Validation of analytical procedures: Text and methodology Q2(R1)*. ICH.
- [12] Keith, L. H., Gron, L. U., & Young, J. L. (2007). Green analytical methodologies. *Chemical Reviews*, 107(6), 2695–2708.
- [13] Kolpin, D. W., Furlong, E. T., Meyer, M. T., Thurman, E. M., Zaugg, S. D., Barber, L. B., & Buxton, H. T. (2002). Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000: A national reconnaissance. *Environmental Science & Technology*, 36(6), 1202–1211.
- [14] Miller, J. N., & Miller, J. C. (2018). *Statistics and chemometrics for analytical chemistry* (7th ed.). Pearson.
- [15] Pena-Pereira, F., Wojnowski, W., & Tobiszewski, M. (2020). AGREE — Analytical GREENness metric approach and software. *Analytical Chemistry*, 92(14), 10076–10082.
- [16] Prat, D., Wells, A., Hayler, J., Sneddon, H., McElroy, C. R., Abou-Shehadeh, S., & Dunn, P. J. (2016). CHEM21 selection guide of classical- and less classical-solvents. *Green Chemistry*, 18(1), 288–296.
- [17] Płotka, J., Tobiszewski, M., Sulej, A. M., Kupka, M., Górecki, T., & Namieśnik, J. (2013). Green chromatography. *Journal of Chromatography A*, 1307, 1–20.
- [18] Płotka-Wasyłka, J. (2018). A new tool for the evaluation of the analytical procedure: Green Analytical Procedure Index. *Talanta*, 181, 204–209.

-
- [19] Ribeiro, C., Ribeiro, A. R., Maia, A. S., Gonçalves, V. M. F., & Tiritan, M. E. (2014). New trends in sample preparation techniques for environmental analysis. *Critical Reviews in Analytical Chemistry*, 44(2), 142–185.
- [20] Sanganyado, E., Lu, Z., Fu, Q., Schlenk, D., & Gan, J. (2017). Chiral pharmaceuticals: A review on their environmental occurrence and fate processes. *Water Research*, 124, 527–542.
- [21] Shaaban, H., & Górecki, T. (2015). Current trends in green liquid chromatography for the analysis of pharmaceutically active compounds in the environmental water compartments. *Talanta*, 132, 739–752.
- [22] Snyder, L. R., Kirkland, J. J., & Dolan, J. W. (2010). *Introduction to modern liquid chromatography* (3rd ed.). Wiley.
- [23] Ternes, T. A. (1998). Occurrence of drugs in German sewage treatment plants and rivers. *Water Research*, 32(11), 3245–3260.
- [24] Tobiszewski, M., Mechlińska, A., & Namieśnik, J. (2010). Green analytical chemistry — Theory and practice. *Chemical Society Reviews*, 39(8), 2869–2878.
- [25] Welch, C. J., Wu, N., Biba, M., Hartman, R., Brkovic, T., Gong, X., Helmy, R., Schafer, W., Cuff, J., Pirzada, Z., & Zhou, L. (2010). Greening analytical chromatography. *TrAC Trends in Analytical Chemistry*, 29(7), 667–680.