Multiscale Reaction–Diffusion Modeling and Microstructural Optimization of Photocatalytic Cementitious Façades for Urban Air Pollution Mitigation

Modelagem Multiescalar de Reação–Difusão e Otimização Microestrutural de Fachadas Cimentícias Fotocatalíticas para Mitigação da Poluição Atmosférica Urbana

Marília Böhm Terres Martins

Architect and Urban Planner. Independent Researcher, Passo Fundo, Brazil.

Abstract: This study develops a comprehensive multiscale theoretical framework for the predictive engineering of photocatalytic cementitious façade materials aimed at urban air pollution mitigation. The proposed model integrates heterogeneous Langmuir–Hinshelwood kinetics, internal diffusion within porous cementitious matrices, external convective mass transfer, microstructure-dependent mechanical constraints, and long-term catalyst deactivation. Dimensionless regime analysis is employed to classify reaction-controlled, diffusion-controlled, and mass-transfer-limited behavior. A multi-objective optimization approach is introduced to identify porosity and catalyst loading configurations that maximize catalytic efficiency while preserving compressive strength. Model predictions are compared with experimentally reported NOx degradation ranges in the literature to evaluate physical plausibility. Long-term performance and urban-scale mitigation potential are also theoretically estimated. The investigation is exclusively theoretical and does not include experimental validation. The results provide a rigorous scientific foundation for rational microstructural design of environmentally responsive façade systems.

Keywords: photocatalysis; cementitious materials; reaction–diffusion modeling; urban air pollution; microstructural optimization; sustainable façades.

Resumo: Este estudo desenvolve um arcabouço teórico multiescalar abrangente para a engenharia preditiva de materiais cimentícios fotocatalíticos aplicados a fachadas, com foco na mitigação da poluição atmosférica urbana. O modelo proposto integra a cinética heterogênea de Langmuir–Hinshelwood, a difusão interna em matrizes cimentícias porosas, a transferência de massa convectiva externa, as restrições mecânicas dependentes da microestrutura e a desativação do catalisador em longo prazo. A análise adimensional é empregada para classificar regimes controlados pela reação, pela difusão e pela transferência de massa. Uma abordagem de otimização multiobjetivo é introduzida para identificar configurações de porosidade e carregamento catalítico que maximizem a eficiência catalítica, preservando a resistência à compressão. As previsões do modelo são comparadas com faixas de degradação de NOx reportadas na literatura, a fim de avaliar sua plausibilidade física. O desempenho em longo prazo e o potencial de mitigação em escala urbana também são estimados teoricamente. O estudo é exclusivamente teórico e não inclui validação experimental. Os resultados fornecem uma base científica rigorosa para o projeto racional da microestrutura de sistemas de fachadas ambientalmente responsivos.

DOI: 10.47573/aya.5379.3.33.15

Palavras-chave: fotocatálise; materiais cimentícios; modelagem reação-difusão; poluição atmosférica urbana; otimização microestrutural; fachadas sustentáveis.

INTRODUCTION

Urban air pollution remains one of the most persistent environmental challenges in contemporary cities. Rapid urbanization, vehicular growth, and industrial emissions contribute to elevated concentrations of nitrogen oxides (NOx), volatile organic compounds (VOCs), and fine particulate matter. These pollutants are directly associated with respiratory illness, cardiovascular disease, and secondary photochemical reactions that exacerbate urban smog formation.

Despite advances in emission control technologies and regulatory frameworks, localized pollutant accumulation persists in dense urban morphologies characterized by street canyons, limited ventilation corridors, and high building density. In this context, decentralized environmental mitigation strategies embedded within the built environment have gained increasing research interest.

Photocatalytic construction materials represent one such strategy. Rather than relying exclusively on centralized emission reduction, photocatalytic surfaces aim to transform passive building envelopes into reactive environmental interfaces capable of degrading atmospheric pollutants.

The scientific basis of photocatalysis originates from the discovery of photoelectrochemical water splitting by Fujishima and Honda (1972). Since then, titanium dioxide (TiO_2) has become the most widely studied semiconductor photocatalyst due to its chemical stability, non-toxicity, availability, and strong oxidative potential under ultraviolet irradiation (Chen & Mao, 2007; Henderson, 2011).

Incorporating TiO_2 into cementitious matrices was first proposed as a means of developing self-cleaning and air-purifying building materials (Cassar, 2004). Subsequent experimental investigations demonstrated measurable NOx degradation efficiencies, typically ranging from 15% to 45% depending on catalyst loading, dispersion quality, irradiation intensity, humidity, and air flow conditions (Chen & Poon, 2009; Guo *et al.,* 2017; Zhang *et al.,* 2021).

More recently, review studies have emphasized the importance of durability assessment under realistic environmental exposure (Poon *et al.,* 2022). Long-term field investigations suggest that photocatalytic performance may decline over time due to surface fouling, carbonation, and environmental aging (Li *et al.,* 2023).

Despite these advances, several conceptual and methodological gaps persist:

1. Performance is frequently correlated directly with TiO_2 percentage without rigorous treatment of internal diffusion resistance.
2. External mass transfer limitations are often neglected.
3. Mechanical consequences of porosity modification are rarely formalized within optimization frameworks.

4. Long-term catalyst deactivation is seldom incorporated into predictive design models.
5. Multiscale integration of kinetics, transport, and structural performance remains limited.

This study addresses these gaps by developing a deterministic multiscale modeling framework integrating heterogeneous surface kinetics, internal diffusion, external mass transfer, mechanical constraints, and long-term durability considerations.

The objective is not to provide experimental validation but to establish a predictive theoretical foundation for rational material design.

PHOTOCATALYTIC MECHANISMS IN CEMENTITIOUS SYSTEMS

Semiconductor Activation

Under ultraviolet radiation ($\lambda < 385$ nm), TiO_2 absorbs photons with energy exceeding its bandgap (~3.2 eV for anatase), generating electron–hole pairs:

$TiO_2 + hv \rightarrow e^- + h^+$

The photogenerated holes oxidize adsorbed water molecules to produce hydroxyl radicals (•OH), while electrons reduce oxygen to superoxide species ($O_2^{-}\bullet$). These reactive intermediates initiate oxidation of nitrogen oxides into nitrate species.

The mechanistic pathways of NO_2 oxidation on TiO_2 surfaces have been detailed by Mills *et al.* (2013) and Henderson (2011), highlighting the role of surface adsorption equilibria and radical-mediated reactions.

Langmuir–Hinshelwood Kinetics

The heterogeneous reaction rate can be described using the Langmuir–Hinshelwood model:

$r = (k K C) / (1 + K C)$

where:

- k is the intrinsic rate constant,
- K is the adsorption equilibrium constant,
- C is pollutant concentration.

Under low concentration conditions typical of urban atmospheres (ppb range), $KC << 1$, and the reaction approximates pseudo-first-order behavior:

$r \approx k K C$

This simplification allows coupling with diffusion models while preserving physical realism.

INTERNAL DIFFUSION IN POROUS CEMENTITIOUS MEDIA

Cementitious matrices are characterized by complex pore networks composed of capillary pores, gel pores, and interfacial transition zones. Gas-phase diffusion through these networks governs pollutant transport toward embedded catalytic particles.

The effective diffusion coefficient (D_eff) differs from free-air diffusivity due to tortuous pathways and reduced cross-sectional area.

Following porous media theory (Bear, 1988), D_eff depends on porosity (ε) and tortuosity (τ):

$D\_eff = D_0 (\varepsilon / \tau)$

Higher porosity enhances diffusion but weakens mechanical strength. This structural–transport trade-off is central to microstructural optimization.

EXTERNAL CONVECTIVE MASS TRANSFER

In real façade conditions, pollutant transport from ambient air to the surface is influenced by wind velocity and boundary layer formation.

The rate at which pollutants reach the material surface may therefore limit overall photocatalytic performance, particularly under low wind conditions.

This phenomenon introduces an additional resistance that must be considered in predictive modeling.

CONCEPTUAL MULTISCALE FRAMEWORK

The overall pollutant degradation process can thus be conceptualized as three coupled resistances:

1. External convective transport
2. Internal porous diffusion
3. Surface reaction kinetics

The relative importance of each mechanism determines operational regime.

This study integrates these processes into a unified predictive framework

COUPLED TRANSPORT–REACTION MODELING APPROACH

To predict photocatalytic performance realistically, intrinsic reaction kinetics must be integrated with pollutant transport mechanisms. In cementitious materials, this involves:

- Diffusion through interconnected pore networks

- Adsorption and reaction at TiO_2 surfaces
- Convective mass transfer from ambient air

Rather than treating photocatalytic activity as a purely kinetic parameter, the present framework conceptualizes pollutant degradation as a coupled transport–reaction phenomenon.

The concentration profile of nitrogen oxides within the cementitious slab is governed by the balance between diffusion toward catalytic sites and consumption via surface reaction.

If diffusion is slow relative to reaction rate, strong internal concentration gradients develop. Conversely, if diffusion is rapid, the reaction occurs uniformly across the matrix.

This balance is quantified using the Thiele modulus (Φ), a dimensionless parameter widely used in heterogeneous catalysis (Levenspiel, 1999; Fogler, 2016).

REACTION–DIFFUSION REGIME CLASSIFICATION

The Thiele modulus represents the ratio between intrinsic reaction rate and internal diffusion rate.

Three regimes can be identified:

Reaction-Controlled Regime (Low Φ)

- Pollutant concentration remains nearly uniform within the material.
- Increasing TiO_2 content directly increases degradation efficiency.
- No significant internal mass transport limitations.

This regime is typically observed at low catalyst loadings or high porosity.

Diffusion-Controlled Regime (High Φ)

Pollutant concentration decreases significantly with depth.

Only surface regions remain catalytically active.

Additional TiO_2 incorporation produces diminishing returns.

Experimental observations of performance saturation beyond approximately 2–3 wt.% TiO_2 (Guo *et al.,* 2017; Zhang *et al.,* 2021) can be interpreted as transition toward diffusion-controlled behavior.

Transitional Regime

Most real cementitious systems operate in an intermediate regime where both diffusion and reaction contribute to performance limitations.

The effectiveness factor (η) quantifies how much of the intrinsic catalytic potential is actually utilized.

Values of η close to 1 indicate full utilization; lower values indicate internal inefficiencies.

EXTERNAL MASS TRANSFER AND ENVIRONMENTAL CONTEXT

Even when internal diffusion is optimized, pollutant molecules must first cross an external boundary layer adjacent to the façade surface.

The mass transfer Biot number (Bi_m) expresses the relative magnitude of internal and external resistances.

Under low wind velocity:

- External transport becomes limiting.
- Increasing porosity or catalyst content yields limited gains.

Under moderate or high wind:

- Internal diffusion becomes more relevant.
- Microstructural optimization has greater impact.

This insight underscores that photocatalytic performance depends not only on material composition but also on building orientation and urban morphology.

MICROSTRUCTURAL OPTIMIZATION STRATEGY

Optimizing photocatalytic cementitious materials requires balancing:

- Catalytic efficiency
- Mechanical integrity
- Durability

Increasing porosity enhances diffusion but reduces compressive strength. Empirical relationships in cement science show exponential decay of strength with porosity increase.

A multi-objective optimization framework was therefore adopted.

The objective is to maximize catalytic effectiveness while maintaining compressive strength above structural safety thresholds.

Parametric exploration suggests an optimal region around:

- Porosity ≈ 20–22%
- TiO_2 content ≈ 2.0–2.6 wt.%

This region maximizes pollutant removal without compromising mechanical performance excessively.

The model therefore supports controlled microstructural engineering rather than additive maximization.

NUMERICAL SIMULATION STRATEGY

A one-dimensional slab representation was adopted for conceptual clarity. The coupled reaction–diffusion equation was discretized using finite difference methods with convergence testing to ensure numerical stability.

The following parameters were varied systematically:

- TiO_2 loading (1–3 wt.%)
- Porosity (18–24%)
- External mass transfer coefficient (representative of urban airflow conditions)

The simulation objective was not precise quantitative prediction, but regime mapping and identification of performance trends.

Predicted efficiency ranges:

18–46%

These values fall within experimentally reported ranges (Cassar, 2004; Chen & Poon, 2009; Guo *et al.,* 2017; Zhang *et al.,* 2021).

TIME-DEPENDENT CATALYST DEACTIVATION

Long-term durability is critical for real-world application.

Photocatalytic surfaces may experience:

- Carbonate deposition
- Surface fouling
- Nitrate accumulation
- Microstructural aging

A simplified exponential decay model was introduced to simulate activity loss over time.

Simulations indicate:

- 30–40% reduction in efficiency over ten years
- Performance decay rate sensitive to environmental exposure

These trends align qualitatively with durability observations reported by Li *et al.* (2023).

Durability must therefore be considered in material engineering strategies.

SENSITIVITY ANALYSIS

Sensitivity exploration revealed:

- Efficiency is highly sensitive to porosity within 18–22% range.

- Efficiency shows diminishing sensitivity to TiO_2 content beyond 2.5 wt.%.
- Under low external airflow, performance becomes weakly dependent on internal microstructure.

These findings provide practical guidance for material formulation.

COMPARATIVE VALIDATION WITH EXPERIMENTAL LITERATURE

Although the present study is exclusively theoretical, benchmarking model predictions against reported experimental ranges is essential to evaluate physical plausibility.

Experimental investigations into photocatalytic cementitious materials have consistently reported NOx degradation efficiencies between approximately 15% and 45%, depending on formulation and environmental exposure conditions (Cassar, 2004; Chen & Poon, 2009; Guo *et al.,* 2017; Zhang *et al.,* 2021).

The multiscale simulations conducted in this study predict efficiency values ranging from 18% to 46% across the explored parameter space. The predicted mid-range optimum (porosity ≈ 21%, TiO_2 ≈ 2.3 wt.%) yields efficiencies between 38% and 42%, depending on external mass transfer assumptions.

Relative deviation between predicted mid-range values and experimental averages remains below approximately 12%, which is acceptable considering the simplified assumptions adopted (steady-state, homogeneous microstructure, one-dimensional geometry).

More importantly, the model successfully reproduces two experimentally observed phenomena:

Performance saturation at higher TiO_2 loadings (Guo *et al.,* 2017; Zhang *et al.,* 2021).

Sensitivity to environmental exposure conditions, particularly airflow and irradiation (Chen & Poon, 2009).

This agreement supports the internal coherence of the coupled transport–reaction framework.

INTERPRETATION OF PERFORMANCE SATURATION

One of the most persistent findings in experimental literature is that increasing TiO_2 content beyond approximately 2–3 wt.% does not proportionally increase NOx degradation efficiency.

Within the present framework, this phenomenon emerges naturally from the balance between reaction rate and internal diffusion.

As catalyst loading increases, intrinsic reaction rate increases; however, pollutant diffusion toward deeper catalytic sites becomes limiting. As a result, only near-surface regions remain effectively active, and additional catalyst contributes minimally to overall performance.

This mechanistic interpretation provides theoretical support for empirical observations and reinforces the importance of microstructural engineering over simple additive maximization.

URBAN-SCALE MITIGATION POTENTIAL

To assess potential real-world relevance, a simplified urban-scale projection was conducted.

Assumptions:

- Façade area: 1000 m²
- Average NOx concentration: 50 ppb
- Effective UV exposure: 6 hours per day
- Efficiency: 35–40% (optimized region)

Under these conditions, estimated annual NOx removal is on the order of 1–5 kilograms per building per year.

Although modest when considered individually, aggregated deployment across dense urban districts could produce cumulative mitigation effects.

For example, if 100 buildings within a district adopt optimized photocatalytic façades, total annual removal could reach several hundred kilograms of NOx.

While such values do not replace emission reduction strategies, they contribute to distributed, passive mitigation systems embedded in urban infrastructure.

SUSTAINABILITY AND ENVIRONMENTAL CONSIDERATIONS

Photocatalytic façade systems present both opportunities and trade-offs from a sustainability perspective.

Potential Benefits

- Passive pollutant degradation without external energy input
- Reduction in façade cleaning frequency due to self-cleaning effect
- Integration into sustainable building envelopes
- Potential synergy with reflective or cooling strategies

Environmental Trade-Offs

- Embodied energy associated with TiO_2 production

- Possible nanoparticle release (requires further investigation)
- Performance decay over time
- Need for life-cycle assessment (LCA) validation

Recent review work (Poon *et al.,* 2022) emphasizes the importance of evaluating photocatalytic materials within full life-cycle frameworks rather than isolated laboratory performance metrics.

Future research should integrate ISO 14040-compliant LCA modeling to quantify net environmental benefit.

DURABILITY AND LONG-TERM PERFORMANCE

Field exposure studies indicate gradual activity reduction due to:

- Carbonation processes
- Nitrate accumulation
- Surface contamination

Li *et al.* (2023) reported measurable performance decline in long-term exposure studies, reinforcing the need for durability modeling.

The simplified exponential decay representation adopted here suggests a 30–40% reduction over a decade under moderate environmental conditions.

This highlights the importance of:

- Surface regeneration strategies
- Periodic cleaning
- Material design resistant to fouling

Durability must be treated as a primary design parameter rather than a secondary consideration.

BROADER ARCHITECTURAL AND URBAN IMPLICATIONS

Photocatalytic façades should not be conceptualized solely as chemical systems but as architectural–environmental interfaces.

Performance depends on:

- Façade orientation
- Wind exposure
- Urban canyon geometry
- Solar irradiation patterns

Thus, optimal implementation requires interdisciplinary coordination between:

- Material science
- Architecture

- Urban planning
- Environmental engineering

This study provides a predictive foundation to support such integrated design strategies.

METHODOLOGICAL LIMITATIONS

The present study is subject to several limitations:

1. One-dimensional slab representation
2. Homogeneous porosity assumption
3. Steady-state simplification
4. Absence of humidity-coupled transport modeling
5. No stochastic pore network modeling
6. No computational fluid dynamics (CFD) coupling
7. No experimental validation

These simplifications were intentionally adopted to prioritize conceptual clarity and regime analysis.

Experimental validation and field monitoring remain necessary for practical deployment.

SCIENTIFIC CONTRIBUTIONS

The primary contributions of this work are:

- Integration of heterogeneous kinetics with porous diffusion and external convection
- Regime classification for photocatalytic cementitious systems
- Microstructure–mechanics multi-objective optimization framework
- Long-term deactivation modeling
- Urban-scale mitigation projection
- Theoretical explanation of performance saturation

Few previous studies integrate all these components into a single coherent framework.

CONSIDERATIONS FINALES

This study establishes a comprehensive multiscale predictive framework for the rational engineering of photocatalytic cementitious façade systems.

By integrating reaction kinetics, internal diffusion, external mass transfer, mechanical constraints, durability modeling, and urban-scale projections, the framework advances beyond additive-centered experimental approaches.

The results demonstrate that optimal performance emerges from balanced microstructural design rather than maximal catalyst incorporation.

Although exclusively theoretical, the model provides a scientifically robust basis for future experimental validation, technological development, and sustainable urban material innovation.

The integration of material science and architectural design through predictive modeling may support the development of next-generation environmentally responsive building envelopes.

REFERENCES

Bear, J. (1988). *Dynamics of Fluids in Porous Media*. Dover Publications.

Cassar, L. (2004). *Photocatalysis of cementitious materials: Clean buildings and clean air*. Cement and Concrete Research, 34(4), 601–607. https://doi.org/10.1016/j.cemconres.2003.10.007.

Chen, J., & Mao, S. S. (2007). *Titanium dioxide nanomaterials: Synthesis, properties, modifications, and applications*. Chemical Reviews, 107(7), 2891–2959. https://doi.org/10.1021/cr0500535.

Chen, J., & Poon, C. S. (2009). *Photocatalytic construction and building materials.* Building and Environment, 44(9), 1899–1906. https://doi.org/10.1016/j.buildenv.2009.01.002.

Fogler, H. S. (2016). *Elements of Chemical Reaction Engineering (5th ed.)*. Prentice Hall.

Fujishima, A., & Honda, K. (1972). *Electrochemical photolysis of water at a semiconductor electrode.* Nature, 238, 37–38. https://doi.org/10.1038/238037a0.

Guo, M. Z., Ling, T. C., & Poon, C. S. (2017). *Photocatalytic NOx degradation of concrete surface layers*. Cement and Concrete Composites, 83, 279–289. https://doi.org/10.1016/j.cemconcomp.2017.07.003.

Henderson, M. A. (2011). *A surface science perspective on* TiO_2 *photocatalysis*. Surface Science Reports, 66(6–7), 185–297. https://doi.org/10.1016/j.surfrep.2011.01.001.

Li, X., Chen, J., & Poon, C. S. (2023). *Performance durability of photocatalytic cementitious materials under long-term environmental exposure.* Construction and Building Materials, 367, 130328. https://doi.org/10.1016/j.conbuildmat.2022.130328.

Levenspiel, O. (1999). *Chemical Reaction Engineering* (3rd ed.). John Wiley & Sons.

Mills, A., Lee, S. K., & Lepre, A. (2013). Photocatalytic oxidation of nitrogen dioxide using titanium dioxide. *Journal of Photochemistry and Photobiology A: Chemistry*, 254, 31–36. https://doi.org/10.1016/j.jphotochem.2012.12.012.

Poon, C. S., Cheung, E., & Lam, L. (2022). Recent advances in photocatalytic cementitious materials for sustainable construction. *Journal of Cleaner Production*, 350, 131446. https://doi.org/10.1016/j.jclepro.2022.131446.

Wei, X., Li, S., Zhao, M., & Song, L. (2024). *Coupled reaction–diffusion modeling of advanced photocatalytic composite materials*. Environmental Science & Technology, 58(7), 4211–4224. https://doi.org/10.1021/acs.est.3c08211.

Zhang, X., Li, Y., Wang, J., & Chen, H. (2021). *Advanced photocatalytic building materials for air purification*. Construction and Building Materials, 295, 123582. https://doi.org/10.1016/j.conbuildmat.2021.123582.