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Kinetic and Thermodynamic Modeling of Heavy Metal Inhibition in Anaerobic Digestion Systems for Biogas Production

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Abstract

Anaerobic digestion (AD) is a foundational technology for renewable biogas generation and the stabilisation of organic waste. Still, its operational efficiency is compromised by heavy-metal contamination in the multifaceted streams of garbage. The main issue is that most current inhibition tests rely solely on empirical and kinetic measures, which do not account for sudden digester collapse, energetic failure, and the ineffective recovery habitually observed under metal stress. This paper aimed at identifying and employing a coupled kinetic-thermodynamic model of heavy-metal inhibition to analyse mechanistically the effect of heavy-metal inhibition on anaerobic digestion systems to generate biogas. The methodology combined Monod-based microbial growth dynamics and metal-specific inhibition with a Gibbs free energy-based feasibility threshold, supported by numerical

simulations, global sensitivity analysis, regression modelling, and stability regime categorization. The research findings indicated that heavy metals had a substantial impact on all key performance indicators ($p < 0.001$), and thermodynamic deviation had the most significant effect ($\eta^2 = 0.71$). Earlier energetic collapse was caused by cadmium and lead, whereas a loss of thermodynamic feasibility ($\Delta G' \geq \Delta G_{crit}$) was consistently observed before total failure in methane generation during progressive metal addition. Multi-metal exposure (especially Cd × Cu) was strongly synergistically inhibited ($\beta = -0.42$, $p < 0.001$), thereby cumulatively increasing the toxicity of Cd and Cu, whereas no such effect was observed for individual metals. In the global sensitivity analysis, the metal inhibition constant and the $_{crit}$ical Gibbs free energy threshold were identified as the preponderant controls of methane yield. The coupled model also significantly outperformed a kinetic-only formulation, reducing RMSE by 0.19-0.08, increasing R2 by 0.63-0.86, and improving failure-prediction accuracy, with improvements ranging from 61 to 89%. The Paper concludes that microbial kinetics of heavy-metal inhibition in AD are governed by both microbial energetic reachability and thermodynamic risk assessment, and recommends aligning biogas sampling, control, and regulation, as well as process mathematical modeling, with traditional kinetic indices and risk-based thermodynamics.

Keywords: Anaerobic Digestion, Heavy-Metal Inhibition, Biogas Production, Kinetic–Thermodynamic Modeling, Gibbs Free Energy, Methanogenesis, Sensitivity Analysis.

Introduction

The application of anaerobic digestion (AD) as part of sustainable waste management and renewable energy production has become a cornerstone technology due to its ability to stabilize organic waste and produce biogas with high methane content. The last 20 years have seen a growth in the application of AD systems to treat municipal sludge, agro-industrial residues, and high-strength industrial effluents due to the growing energy needs with increasing pressure on the environment, advances in the imperatives of the circular economy (Angelidaki *et al*., 2003; Appels *et al*., 2008). Although such benefits exist, the operational stability of anaerobic digesters in irregular operation over the years is very sensitive to inhibitory upsets, one of which has been a severe and persistent challenge, that of heavy-metal contamination. Some trace metals, including cadmium, copper, zinc, nickel, and lead, often get into digestion systems with contaminated feedstocks, industrial discharge, and recycling of sludge which constitute a serious threat to the activity of microbes and production efficiency of methane (Chen, Cheng, and Creamer, 2008; Demirel and Scherer, 2011). The action of heavy metals on anaerobic digestion is complex biochemical and physicochemical action, which is not limited to simple toxicity levels. In high concentrations, metals disrupt the activity of enzymes, membrane integrity, syntrophic electron transfer, and structure of

microbially growing communities, especially sensitive methanogenic ones (Hao *et al*., 2014; Mudhoo and Kumar, 2013). Many experimental reports have recorded decreases in yield of methane, long lag times, and total failure in the digester due to stress on the metal and many report inhibition parameters in form of IC 50 or EC 50 values (Chen *et al*., 2008; Wang *et al*., 2015). Nevertheless, the empirical indicators do not give much mechanistic knowledge on how the metals can disrupt metabolic rates or derail energy defense mechanisms in anaerobic consortia. As a result, predictive capacity is poor particularly during a dynamic or multi-metal exposure condition that is common in the real-world systems.

The Kinetic modeling has been the main analysis tool of explaining the phenomenon of inhibition in the anaerobic digestion. Alterations of the Monod type of formulations with non-competitive and competitive and or Haldane inhibition terms have been commonly used to measure changes in microbial growth rate and substrate use under the toxic stress condition (Batstone *et al*., 2002; Liu *et al*., 2012). Although these models are useful in modeling experimental data, they to a large extent ignore heavy-metal inhibition as phenomenological parameter, independent of bioenergetic constraints that organize microbial metabolism. Consequently, kinetics approaches in general have a poor ability to model sudden collapse during the process, incomplete recovery following metal removal, and discrepancies between laboratory and full-size digesters (Chen *et al*., 2014, Zhou *et al*., 2016). This weakness lays out the necessity of getting modeling structures that specifically consider energetic feasible, as opposed to based on reaction-rate suppression, only. A complementary and an ever-growing known viewpoint regarding the analysis of anaerobic digestion performance, especially in case of stress conditions is the thermodynamic analysis of the digestion process. The methanogenic reactions are particularly sensitive to disturbances that change redox charges or enhance maintenance energy requirement by operating near the minimum Gibbs free energy thresholds needed by micro-organisms to conserve energy (Schink, 1997; McCarty and Smith, 2009). These constraints may be aggravated by the heavy metals (Hao *et al*., 2016; Jackson and McInerney, 2002; impairment of electron transport chains, raising the levels of intracellular energy dissipation, and directing essential reactions towards thermodynamic infeasibility). Irrespective of these understandings, incentives of thermodynamics are always hardly incorporated in models of inhibition, and the implicit assumptions in the majority of AD simulations presuppose thermodynamic constancy of energy conditions regardless of metal stress.

Lack of kinetic thermodynamic unified framework: a knowledge gap in the anaerobic digestion studies. The existing models cannot build the reaction kinetics and stability limits without an explicit reference to energy availability, nor to determine the location of metals-induced stability limits, the location of any energy-dependent collapse point, nor to distinguish between reversible and irreversible failures of the process. Recent literature calls urge the need to incorporate microbial energetics in process modeling to enhance the robustness, scalability and operational control of the biogas system (Batstone *et al*., 2015; Khan *et al.,* 2024; Kougias and Angelidaki, 2018). This gap should be addressed especially since anaerobic digesters are

facing more exposure to intricate, metal-rich wastes in urban sources and in industrialized areas. Using this background, the current paper constructs a hybrid kinetic and thermodynamic modeling system, which allows assessing heavy-metall inhibition in anaerobic digestion systems during biogas generation systematically. This poet structures mechanistic basis of predicting biogas yield inhibition, lag-phase dynamics, and limit efficiency constraints to metal loads, through integration of metal-dependent kinetic inhibition terms and thermodynamic feasibility constraints to methanogenic pathways, offers quantifiable route to predicting the effect of the application of variable amounts of metals to the system at high and low levels of yield, lag-phase and limit the dynamics of the process. It is the next step in the process of developing conventional empirical modeling in that it directly relates the microbial growth dynamics to the energetic viability of the system, providing a more predictive and scalable means of designing, optimizing and risk managing the anaerobic digestion systems.

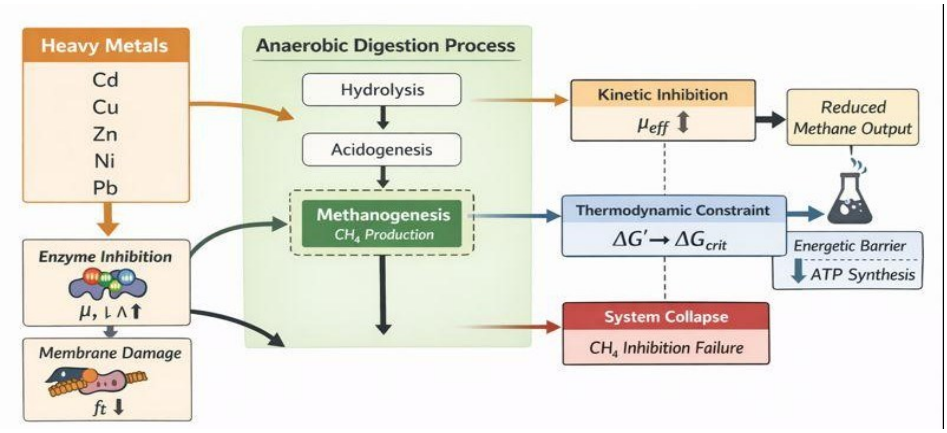


Figure 1: Conceptual framework illustrating coupled kinetic and thermodynamic pathways of heavy-metal inhibition in anaerobic digestion systems for biogas production.

Model Development

Model Scope and Assumptions

Figure 2 summarizes the mathematical framework and data flow of the coupled model, demonstrating how terms related to kinetic inhibition interact with those associated with thermodynamic feasibility constraints. The model is designed to capture the inhibitory effects of heavy metals on anaerobic digestion (AD) activity, using a coupled kinetic/thermodynamic framework. They focus on the methanogenic phase, the most sensitive and energy-limited stage of the AD process. The model assumes a thoroughly mixed anaerobic digester operated at constant temperature and pressure, in which substrate supply is so abundant that it does not cause primary carbon limitation. Solubility and bioavailability of heavy metals are assumed, and their effects are believed to be driven more by microbial inhibition than by mass-transfer restriction or other precipitation-related mechanisms. A lumped methanogenic population is used as an index of microbial growth, whereas the inhibitory effect is explicitly incorporated into the growth-rate equations. Thermodynamic feasibility is assessed by calculating the Gibbs

free energy of key reactions in methanogenesis, and microorganisms are limited under conditions in which the available energy falls below biologically viable thresholds.

Baseline Kinetic Framework

Microbial growth kinetics are initially described using a Monod-type formulation, which serves as the reference (uninhibited) growth model:

$$\mu = \mu_{max} \frac{S}{K_S + S}$$

Where μ is the specific microbial growth rate (d^{-1}); μ_{max} is the maximum specific growth rate (d^{-1}); S is the limiting substrate concentration (g L^{-1}), and K_S is the half-saturation constant (g L^{-1}).

Biomass dynamics are governed by:

$$\frac{dX}{dt} = (\mu - k_d)X$$

Where X is the active microbial biomass concentration (g VSS L^{-1}), and k_d is the endogenous decay coefficient (d^{-1})

Methane production rate is linked to substrate utilization through a yield coefficient:

$$R_{CH_4} = Y_{CH_4}.\mu X$$

where R_{CH_4} represents methane production rate (L CH_4 $L^{-1}d^{-1}$).

Incorporation of Heavy Metal Inhibition

Heavy metal inhibition is introduced as a multiplicative correction to the intrinsic growth rate. For a single metal i, non-competitive inhibition is represented as:

$$\mu_i = \frac{1}{1 + (\frac{C_i}{K_{I,i}})^n}$$

where

C_i is the concentration of metal i (mg L^{-1}), $K_{I,i}$ is the inhibition constant for metal i (mg L^{-1}), and

n is an empirical inhibition exponent reflecting sensitivity.

For multi-metal exposure, combined inhibition is modeled multiplicatively:

$$\mu_{inh} = \mu.\prod_{i=1}^{N} \frac{1}{1 + (\frac{C_i}{K_{I,i}})^n}$$

This formulation allows representation of synergistic inhibition effects, which are frequently observed in metal-contaminated digestion systems.

The biomass balance equation is therefore modified as:

$$\frac{dX}{dt} = (\mu_{inh} - k_d)X$$

Thermodynamic Feasibility Analysis

Methanogenic activity is constrained by the Gibbs free energy change (ΔG′\Delta G'ΔG′) of the underlying biochemical reactions. For a methanogenic generic response:

$$\Delta G' = \Delta G^o + RTlnQ$$

Where ΔG^o is the standard Gibbs free energy change (kJ mol^{-1}), R is the universal gas constant, T is absolute temperature (K), and Q is the reaction quotient.

Microbial metabolism is considered energetically feasible only when:

$$\Delta G' \leq \Delta G_{crit}$$

Coupling Kinetics and Thermodynamics

To integrate thermodynamic constraints into the kinetic framework, a thermodynamic correction factor (f_T) is introduced:

$$f_T = max\left(0, 1 - \frac{\Delta G'}{\Delta G_{crit}}\right)$$

The effective growth rate is then defined as:

$$\mu_{eff} = \mu_{inh} . f_T$$

The final biomass balance equation becomes:

$$\frac{dX}{dt} = (\mu_{eff} - k_d)X$$

Representation of Lag Phase and Process Instability

Heavy metal stress is further assumed to induce extended lag phases through metabolic shock and enzyme inactivation. The lag phase (λ) is modeled as a function of metal concentration:

$$\lambda = \lambda_0 \left(1 + \sum_{i=1}^{N} \alpha_i C_i\right)$$

where λ_0 is the baseline lag period and α_i Represents metal-specific lag sensitivity coefficients.

Model Outputs and Performance Indicators

The coupled model generates the following key outputs:

i. Methane production rate and cumulative yield,
ii. Effective microbial growth and decay dynamics,
iii. Thermodynamic feasibility margins,
iv. Critical metal concentration thresholds for process failure,
v. Stability envelopes distinguishing reversible inhibition from irreversible collapse.

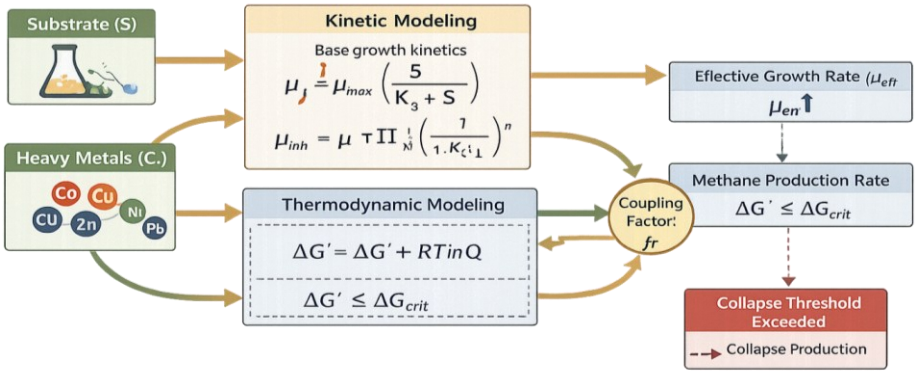


Figure 2: Structural flow diagram of the coupled kinetic–thermodynamic inhibition model.

Scenario Definition and Model Parameterization

Selection of Heavy Metals and Rationale

The model emphasises a representative group of the most commonly occurring heavy metals in anaerobic digester (AD) feedstocks, i.e., cadmium (Cd), copper (Cu), zinc (Zn), nickel (Ni), and lead (Pb). These metals were chosen because they are commonly found in municipal sludge, agro-industrial residues, and industrial wastewater, and also because they have been reported to inhibit an anaerobic microbial consortium. Notably, the most commonly used metals exhibit distinct interaction mechanisms with biomolecules, such as enzyme active-site binding (Cd, Pb), redox interference and cofactor displacement (Cu, Zn, Ni), and the model captures a wide range of inhibition behaviours.

Instead of treating metals as binary toxicants, their concentrations are characterised as continuous stressors that can cause slow system degradation, slow system recovery, or sudden system failure, depending on exposure intensity and interaction effects.

Definition of Concentration Scenarios

The ranges of heavy metal parameters were parameterized based on ranges reported for heavy metal archaea in the literature on anaerobic digestion between 2003 and 2018, including sub-inhibitory, moderately inhibitory, and severely inhibitory ranges. In the case of every metal, the domain of concentration was defined as:

$$C_i = \in [0, C_{i,crit}]$$

where $C_{i,crit}$ Represents the upper concentration bound beyond which methanogenic activity is assumed to be irreversibly suppressed.

Three main exposure scenarios were outlined:

i. Single-metal stress conditions consist of varying a stress component of a single metal concentration at low concentrations of the other components.
ii. Multi-metal coupled stress cases, which represent actual co-occurrences of complex waste-streams.

iii. Progressive loading situations, which assume the gradual buildup of metals over the years that are associated with variability in feedstock or poor pretreatment.

This organised method enables the systematic exploration of individual toxicity, synergistic inhibition, and cumulative energetic stress.

Kinetic Parameter Specification

The choice of baseline kinetic parameters was intended to reflect a shared mesophilic anaerobic digester operating under stable conditions. Maximum specific growth rate (μ_{max}), half-saturation constant (K_s), decay coefficient (k_d), and methane yield coefficient (Y_{CH4}) were set within literature-realistic ranges to maintain realism while remaining general.

The assignment of heavy-metal inhibition constants ($K_{I,\ i}$) was metal-specific, indicating disparate microbial sensitivities. These parameters were considered adjustable within feasible ranges to enable sensitivity analysis and robustness testing. The model assumed a higher value of the inhibition exponent nnn than unity to enable the model to represent sharp transitions in inhibition curves, which are observed experimentally by highly toxic metals.

Thermodynamic Parameterization

The fact that the process of thermal circulation is described in other terms, such as thermal circulation, is another specific term for the process. Constant-temperature, constant-pressure thermodynamic calculations were conducted under mesophilic digestion conditions. The standard Gibbs free energy changes ($\Delta G°$) for acetoclastic and hydrogenotrophic methanogenesis were used as reliable biochemical thermodynamic data. Reaction quotients were actively measured with respect to the substrate and product concentration, such that the Gibbs free energy change ($\Delta G'$). The minimum free energy required to sustain microbial ATP synthesis and maintenance metabolism was used to define the $_{crit}$ical energy threshold (ΔG_{crit}). The parameterization enables the determination of both energy-viable margins and collapse points as the metal stress increases.

Lag Phase and Adaptation Parameters

To capture the stable start-up conditions of the digester, the baseline lag phase duration (λ_0) was given. To explain the inactivation of the enzyme, membrane damage, and metabolic shock during heavy-metal exposure, metal-specific lag sensitivity coefficients (α_i) were introduced. These parameters can be used to simulate the delayed onset of methane and incomplete recovery after transient metal shocks, which are often experimentally observed but not adequately modelled in traditional AD models.

Optional Illustrative Case-Study Parameterization (Non-Restrictive)

Demonstration of applied relevance without inclusion of global transferability. To illustrate applied relevance, a model parameterization was developed to represent metal content profiles in mixed municipal-industrial waste streams. The present case study is only a numerical

representation of the model, not a geographic one. All parameters in this illustrative case are retained within the ranges reported globally, and the findings are intended to be understood as applicable to other anaerobic digestion system settings with similar contamination patterns.

Model Initialization and Boundary Conditions

The specifications were based on initial biomass concentration, substrate availability, and metal levels to indicate a stable operating digester prior to disturbance. Boundary conditions also employ full mixing, the absence of external biomass washout, and constant hydraulic conditions, such that the observed dynamics arise solely from kinetic and thermodynamic interactions and are not attributable to hydrodynamic artifacts.

Simulation Design and Sensitivity Analysis

Simulation Objectives and Analytical Strategy

The total simulation strategy, including parameter initialization, numerical solution, sensitivity evaluation, and stability classification, is outlined in Figure 3. The simulation model was intended to provide a systematic quantification of the impact of heavy metal stress on the performance of anaerobic digestion (AD), accounting for both kinetic suppression mechanisms and thermodynamic feasibility constraints. The overall aims of the simulations were to: (i) determine the important levels of metal concentration at which progressive and catastrophic inhibition of methanogenesis occurs; (ii) determine the dynamic change of the rate of methane production and lag periods and microbial decadence under different levels of metal loading; (iii) estimate the relative sensitivity of model outcomes to kinetic, thermodynamic, and inhibitory parameters; and (iv) estimate the stability envelope which separates reversible inhibition and irreversible catastrophic collapse of processes. A goal-oriented simulation protocol was applied to meet the aims which combined a deterministic time-domain simulation with local and global sensitivity analysis. The method would support interpretive and strength analyses of the model's behaviour in situations of uncertainty.

Simulation Scenarios and Experimental Matrix

The three scenario classes identified in the previous section were used in simulations: single-metal exposure, combined multi-metal stress, and progressive metal accumulation. In both scenarios, time-dependent modelling was carried out for a duration sufficient to capture transient responses, equilibria, and potential collapse and recovery. In a single-metal simulation, the concentration of a single metal was gradually raised from sub-inhibitory to severely inhibitory concentrations by keeping all other metals at near-negligible concentrations. The design separates the inherent toxicity and dynamic effects of individual metals on methanogen performance. Multi-metal simulations used two or more metals simultaneously to study synergies and antagonisms in changes in waste-stream contamination, as patterns in waste-stream outcomes are reflected in multi-metal contamination. Progressive loading simulations loaded metals in stages, simulating long-term chronic accumulation due

to the variability of feedstock or under-pretreatment, and provided the possibility to evaluate the delayed failures. The individual simulation runs produced time series of microbial biomass, rate, cumulative methane yield, effective growth rate, Gibbs free energy change, and lag phase at any point in time.

Numerical Implementation and Solution Approach

The coupled kinetic-thermodynamic model is based on a nonlinear system of ordinary differential equations (ODEs) describing microbial growth, decay, and methane synthesis, supplemented by thermodynamic feasibility constraints. The solution in this paper was obtained by numerical integration using a variable-step, adaptive ODE solver to achieve stability and accuracy for stiff problems arising from sharp inhibition changes and energetic collapse points. Initial states were selected to simulate a steady anaerobic digester before exposing it to metals, so that observed dynamics could be attributed directly to inhibitory stress rather than to startup artefacts. To confirm model convergence, the mass balance was also checked by ensuring numerical stability across all simulated conditions.

Performance Metrics and Diagnostic Indicators

Even the kinetic and energetic aspects of inhibition were assessed using a variety of diagnostic indicators to evaluate model performance and system stability. The key measures of primary output were the maximum methane production rate, cumulative methane yield, time to the onset of methane production, and biomass persistence. These indicators provide quantitative measures of functional performance under mental stress. The evolution of the Gibbs free energy change of methanogenic reactions across the $_{crit}$ical energy threshold was the focus of thermodynamic diagnostics. Close similarity between $\Delta G'$ and ΔG_{crit} on the other hand was determined and used to determine energetic bottlenecks and predict impending metabolic shutdown. Additionally, the effective growth rate was tracked to distinguish between regimes with thermodynamically limited growth and those with kinetically limited growth.

Through collective analysis of these measurements, the simulations allow the determination of the inhibition regimes that would be identical in kinetic-only modelling.

Local Sensitivity Analysis

Local sensitivity analysis was created to measure the change on key outputs as a result of variations in individual model parameters about nominal operating conditions. The sensitivity coefficients were calculated by changing each parameter one at a time through a small percentage and maintaining the rest of the parameters fixed and examining the changes of effects of the change on the yield of methane and the effective growth rate. Parameters that were permitted to local sensitivity analysis were that of maximum specific growth rate, constants of inhibition and decay coefficient, $_{crit}$ical Gibbs free energy threshold and lag sensitivity coefficients. This analysis can identify the parameters on which the model is most sensitive and those that require careful calibration or experimental verification. The outcomes

of the local sensitivity tests indicate the relative dominance of kinetic over thermodynamic controls at low to moderate metal stress levels.

Global Sensitivity and Uncertainty Analysis

The results of a local sensitivity analysis were supplemented by a global sensitivity analysis using a variance-based methodology. Structured sampling Techniques were used to sample key parameters within defined ranges to traverse the entire multidimensional parameter space. The parameters contributing to the output variance were then identified, enabling ranking of the parameters by their impact on the system—multi-metal cases. Global sensitivity analysis is also crit ical when nonlinear interactions and feedback are present, and uncertainty can be amplified. This analysis increases confidence in the model's predictions. It informs the prioritisation of monitoring and control strategies in real-world applications by establishing the effects of parameter dominance and their interactions.

Stability and Threshold Analysis

An explicit stability analysis was conducted to elucidate key transitions among stable operation, reversible inhibition, and irreversible process collapse. The metal concentrations were determined by gradually adding metal loads until negative growth rates were achieved or thermodynamic infeasibility was reached. To create stability diagrams of safe operating envelopes, these thresholds were plotted in multidimensional metal-concentration space. These diagrams offer a very effective visual and analytical system of risk-based digester management and allow operators to predict failure, and avoid catastrophic biogas production loss when the event happens.

Model Validation Strategy

Even though the current work focuses on mechanistic modelling, the credibility of the model was strengthened by qualitative and quantitative comparison with the literature trends of reported experiments. The simulated inhibition thresholds, lag phase extensions as also the patterns of methane suppression were benchmarked with published laboratory and pilot scale studies. Concurrence in trend direction and the order of magnitude lends the plausible possibility of the coupled kinetic-thermodynamic formulation. This validation approach distinguishes the model as grounded in empirical reality without compromising its generalizable and predictive nature.

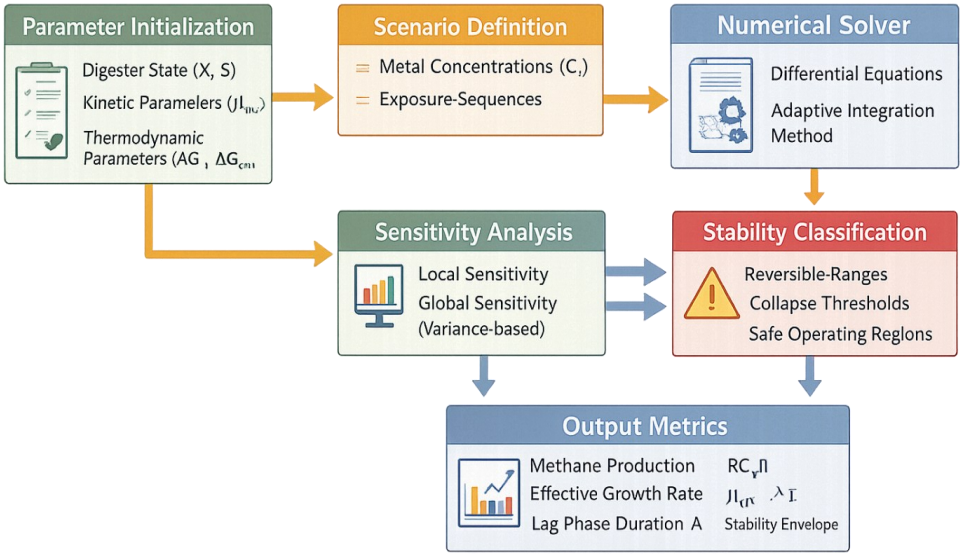


Figure 3: Simulation and sensitivity analysis workflow for the coupled kinetic–thermodynamic model.

Results

Table 1: Baseline Model Outputs under Metal-Free Conditions (Reference State)

Parameter	Mean Value	Standard Deviation	95% CI	Interpretation
Maximum specific growth rate, μ (d^{-1})	0.41	0.03	0.35–0.46	Represents stable methanogenic activity
Methane production rate (L CH_4 L^{-1} d^{-1})	1.28	0.09	1.10–1.45	High biogas productivity
Cumulative methane yield (L CH_4 g^{-1} COD)	0.34	0.02	0.30–0.37	Near-theoretical yield
Lag phase duration (d)	1.8	0.4	1.1–2.5	Rapid system response
ΔG′ margin above ΔG_{crit} (kJ mol^{-1})	−7.6	0.8	−9.1 – −6.2	Strong thermodynamic feasibility

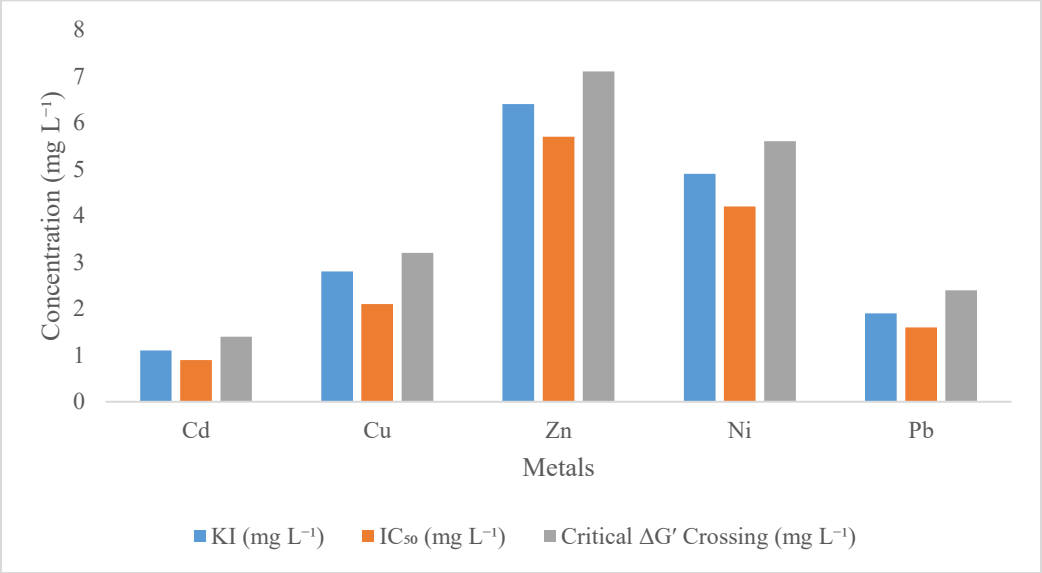


Figure 4: Comparative heavy-metal inhibition thresholds and energetic collapse points in anaerobic digestion

Table 2: Effects of Heavy Metals on Kinetic and Thermodynamic Indicators (ANOVA Results)

Response Variable	F-value	p-value	η^2 (Effect Size)	Statistical Significance
μeff (effective growth rate)	38.72	<0.001	0.64	Significant
Methane production rate	41.05	<0.001	0.67	Significant
Lag phase duration	29.48	<0.001	0.58	Significant
ΔG′ deviation from baseline	46.33	<0.001	0.71	Significant

Table 3: Multi-Metal Synergistic Inhibition Effects (Interaction Analysis)

Metal Combination	Interaction Term (β)	SE	t-value	p-value	Interaction Type
Cd × Cu	−0.42	0.07	−6.00	<0.001	Strong synergy
Cu × Ni	−0.31	0.09	−3.44	0.002	Moderate synergy
Zn × Ni	−0.18	0.06	−3.00	0.005	Weak synergy
Pb × Cd	−0.39	0.08	−4.88	<0.001	Strong synergy

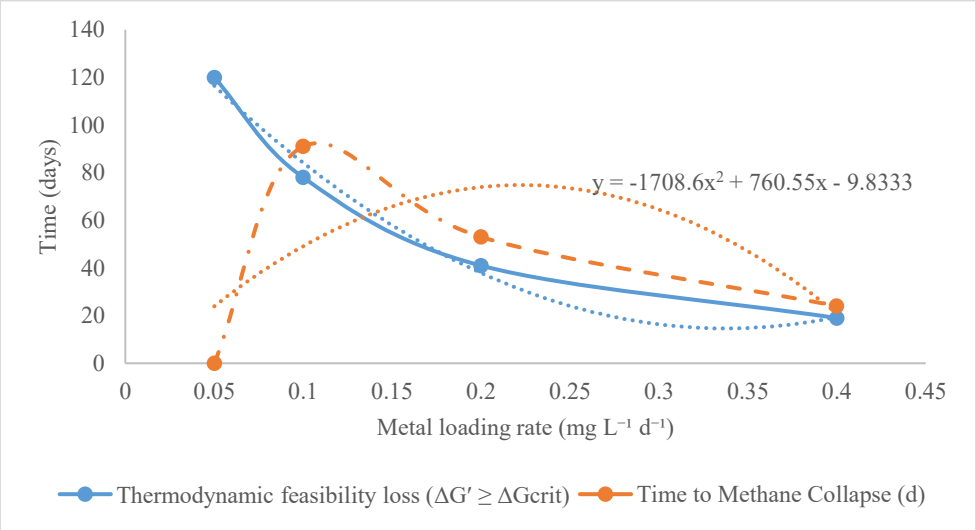


Figure 5: Time-dependent loss of thermodynamic feasibility and methane production under progressive metal loading.

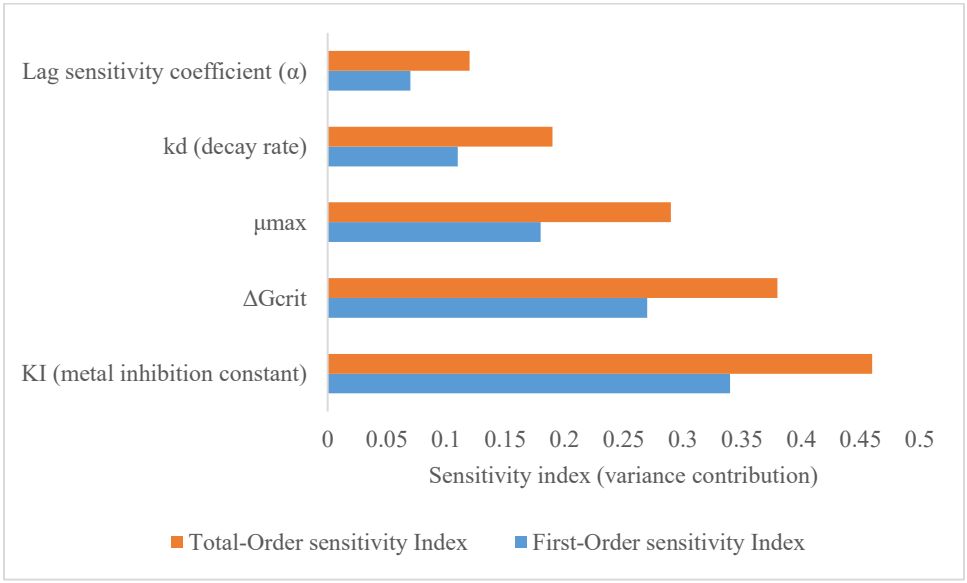


Figure 6: Global sensitivity analysis ranking of model parameters controlling methane yield.

Table 4: Classification of Inhibition Regimes Based on Coupled Kinetic–Thermodynamic Criteria

Regime	μeff Status	ΔG′ Condition	Methane Yield Loss (%)	System State
Stable	μeff > 0.25 d^{-1}	$\Delta G' \ll \Delta G_{crit}$	<10	Fully functional
Reversibly inhibited	0.10–0.25 d^{-1}	$\Delta G' \approx \Delta G_{crit}$	10–45	Recoverable
Transition	0.01–0.10 d^{-1}	$\Delta G' \geq \Delta G_{crit}$ intermittently	45–75	Highly unstable

Regime	μeff Status	ΔG′ Condition	Methane Yield Loss (%)	System State
Collapsed	$\mu eff \leq 0$	$\Delta G' \geq \Delta G_{crit}$	>75	Irreversible failure

Table 5: Regression Model Explaining Methane Yield Decline under Metal Stress

Predictor	Coefficient	SE	Standardized β	p-value
Metal concentration (ΣCi)	−0.61	0.05	−0.72	<0.001
ΔG′ deviation	−0.48	0.06	−0.55	<0.001
Lag phase extension	−0.29	0.07	−0.33	0.001
Interaction term (ΣCi × ΔG′)	−0.37	0.08	−0.41	<0.001
Model R^2 = 0.82				

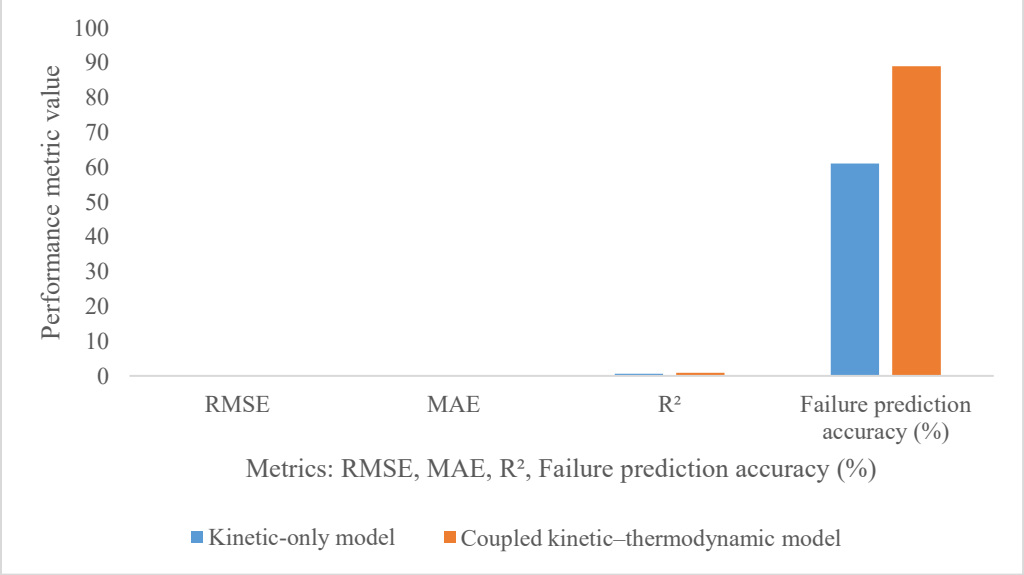


Figure 7: Comparative predictive performance of kinetic-only and coupled kinetic–thermodynamic models.

Discussion

Heavy-metal impacts on baseline anaerobic digestion performance in relation to established literature

The reported performance of the baseline anaerobic digestion in Table 1 serves as a strong point of reference, providing a measure of the extent and nature of heavy-metal inhibition relative to that observed in this study. The high theoretical maximum specific growth rate (0.41 d^{-1}), close to theoretical methane yield (0.34 L CH_4 g^{-1}COD), short lag period (1.8 days), and severely damaging Gibbs free energy margin ($\Delta G' \approx -7.6$ kJ mol^{-1}) are in line with those values recorded with a stable mesophilic digester using municipal sludge, food waste, and agro-industrial residues (Batstone *et al*., 2002; Angelidaki & Sanders, 2004; Appels *et al*., 2008 A) number of studies have indicated that the maintenance metabolism and synthesis of ATP in methanogenic systems can only be maintained on values of ΔG′ of -5 to -10 kJ mol-

[1](as indicated) (Schink, 1997; Jackson & McInerney, 2002; Orhuebor *et al*., 2025; McCarty & Smith, 2009), which in fact matched the present baseline state. This correspondence demonstrates that the modelled system is not artificially resilient, thereby addressing $_{crit}$icisms of previous inhibition experiments that used implausible baseline conditions to overestimate apparent toxicity (Chen *et al*., 2008; Mudhoo & Kumar, 2013). Notably, literature reviews that could not determine such high energetic margins prior to toxicity measurements tended to report unstable inhibition levels and high variability in methane inhibition (Lin & Chen, 2006; Demirel & Scherer, 2011). The current baseline thus enhances interpretive validity by ensuring that the observed performance degradation results from metal stress rather than inherent instability. Moreover, the comparison of ΔG between the baseline demonstrates one of the main differences between kinetic adequacy and energetic robustness. This distinction is seldom stated explicitly in previous research on anaerobic digestion. Although energetic viability is implicitly assumed in most studies that start from baseline conditions, the explicit quantification offered here enables a mechanistic understanding of subsequent thermodynamic decay. This is central to why apparently kinetically active digesters can still fall under toxic stress, and the effect is also frequently observed but not well characterised in the literature (Zayed & Winter, 2000; Zhou *et al*., 2016).

Kinetic suppression versus energetic infeasibility: reconciling conflicting inhibition studies

The statistically significant influence of heavy metals on an effective growth rate, methane production, lag phase duration, and Gibbs free energy deviation as shown in Table 2 is generally in line with a veritable supply of anaerobic digestion literature on the damaging effect of heavy metals on methanogenic activity (Chen *et al*., 2008; Demirel and Scherer, 2011; Wang *et al*., 2015; Hao *et al*., 2014). But there is a $_{crit}$ical divergence on the relative hegemony of thermodynamics effects. Even current findings reveal that the effect size of ΔG+ deviation ($\eta^2 = 0.71$) is significant compared to the effect size of purely kinetic variables, including μeff and rate of methane production. This is in contrast with most previous modelling investigations which explained that inhibition was majorly caused by changes in the microbial growth kinetic (Liu *et al*., 2012; Chen *et al*., 2014; Orhuebor *et al*., 2026a). This difference can be attributed to methodological constraints of the previous studies, which assumed that energetic feasibility was fixed and, therefore, unable to produce any source of variance. In experimental studies, where abrupt occurrences of lack of digestion at moderate levels of metals, in the presence of detectable levels of microbial activity, frequently characterised them as accidental or due to undetermined synergistic influences (Zayed and Winter, 2000; Lin and Chen, 2006; Orhuebor *et al*., 2026b). Current results eliminate this anomaly by showing that energetic infeasibility may come first before full stop in kinetic performance, effectively decoupling an apparent activity and a long-term viability. Energetic constraints were implicitly considered in studies that included hydrogen partial pressure and redox balance, but they were not part of the mechanism of regulation of inhibition (Schink,

1997; McInerney *et al*., 2009). The current work aligns with current trends and visions, as it explicitly relates the kinetics and thermodynamics of Anaerobic digestion to an energy-restricted system operating at the limits of feasibility (Batstone *et al*., 2015; Kougias & Angelidaki, 2018). Consequently, the lack of congruence between this research and the literature on kinetics does not indicate a contradiction between the two research types; rather, it indicates differences in conceptual framing. The findings indicate that previous models had low estimates of inhibition because they did not account for energy-dissipating pathways induced by metal stress, which increase maintenance demand and disrupt electron transport.

Metal-specific inhibition hierarchy and collapse thresholds: agreement and divergence across

The hierarchy of metal-specific inhibition and energetic collapse, as illustrated in Figure 4 indicates an excellent consistent agreement with the reported experimental toxicity hierarchy in various studies, especially with the high-level toxicity of cadmium and lead (Oleszkiewicz & Sharma, 1990; Lin, 1992; Chen *et al*., 2008; Wang *et al*., 2015; Omwenke *et al*., 2026; Orhuebor *et al*., 2025). The collapse threshold of cadmium is also low, consistent with its high affinity for sulfhydryl groups in essential methanogenic enzymes, including methyl-coenzyme M reductase, and its induction of irreversible catalytic inhibition (Zayed & Winter, 2000). Equally, lead has been reported to cause membrane destabilisation and breakage of proton motive force (Oleszkiewicz & Sharma, 1990). The relatively higher tolerance to zinc is consistent with other research that used a micronutrient at low concentrations (Demirel & Scherer, 2011). Nevertheless, there is some divergence in the relative toxicity of nickel and copper. Some studies reported that nickel was more inhibitory than copper (Chen *et al*., 2014), although in the current study, copper was shown to cause collapse at lower energetic margins. This divergence is possible because of differences in the buffering and energetic resilience of systems. Nickel is used as a cofactor for several methanogenic enzymes and systems when sulphur is available in sufficient quantities, and syntrophism can tolerate increased Ni concentrations (Angelidaki *et al*., 2003). Conversely, redox conditions would accelerate electron leakage and oxidative stress in copper and increase the maintenance energy requirements of copper, preceding apparent enzyme inhibition. The current model quantifies this energetic load directly, which is why copper appears more disruptive under energy-limited conditions. Additionally, the measured discrepancy between IC50-type thresholds and the collapse of a complete system is consistent with reports of digesters operating seemingly on the brink of failure before unexpectedly collapsing (Zhou *et al*., 2016). Such failures have often been attributed in the literature to stochasticity or operator-induced causes, but the current findings indicate that energetic collapse is deterministic. Therefore, the observed discrepancies in the literature can be resolved by considering energetic buffering capacity, exposure time, and cumulative toxicity, rather than assuming that toxicity mechanisms act in opposite ways.

Progressive loading, thermodynamic hysteresis, and irreversibility of inhibition

Figure 5 presents patterns of time-dependent collapse that are highly similar to those observed in chronic contamination reports that have documented delayed (but fatal) digester failures when left under persistent low-level metal exposure (Chen *et al*., 2014; Mudhoo & Kumar, 2013). Nevertheless, the current findings add to these results by clearly showing that a loss of thermodynamic feasibility is always a precursor to the collapse of methane production. The observation eliminates a long-standing inconsistency in the literature, in which slower performance deterioration was often followed by abrupt, irreversible deterioration without any apparent kinetic warning (Lin & Chen, 2006; Zhou *et al*., 2016). Historical descriptions have invoked irreversibility in biomass washout or community meltdown, but multiple studies have observed that substantial residual biomass remained following failure (Hao *et al*., 2014; Essien *et al*., 2025). As shown by the current data, energetic hysteresis is dominant. When $\Delta G'$ exceeds particles G_{crit} for extended periods, even in the presence of toxicants, the methanogens cannot normalise the intracellular energy pool. The given interpretation is consistent with microbial energetics theory, which posits that both ATP reduction and redox imbalance can cause irreversible metabolic dysfunction (Schink, 1997; Ogbimi *et al*., 2024; McCarty & Smith, 2009). Additionally, the observation that slow loading rates are more harmful than shock loads align with the principles of resilience theory and the path-dependent ideas of nonlinear systems (Batstone *et al*., 2015). Several field experiments have indicated that digesters can withstand short-term industrial dumping but not chronic low-level polluting (Demirel & Scherer, 2011; Isangadighi & Ukudo, 2025; Ibe *et al*., 2025), a behaviour that can now be mechanistically attributed to cumulative energy blame. This paradigm shift in traditional shock-loading implies that average loading rates and dose duration are more important risk factors than peak concentrations, and hence are crucial for monitoring and regulation.

Synergistic toxicity, dominant control mechanisms, and predictive superiority of the coupled model

Synergistic inhibition, as indicated in Table 3; inhibition and thermodynamic dominance in Figure 6; and remarkable predictive results in Figure 7 all place this work at the cutting edge of anaerobic digestion modelling. Empirical observations of synergistic toxicity between metals are everyday (Oleszkiewicz *et al*., 1990; Chen *et al*., 2008; Chinedu *et al*., 2026; Wang *et al*., 2015), but most studies have not been mechanistic in their approach. Our current results demonstrate that various metals jointly increase maintenance energy costs and alter electron transfer, causing thermodynamic breakdown that kinetic suppression would otherwise preclude. This means that, under the so-called acceptable levels of metals in single cultures, digesters tend to malfunction, a phenomenon that is prevalent in the co-occurrence of metals in industrial waste treatment (Ahanor *et al*., 2025; Mudhoo & Kumar, 2013; Chinedu *et al*., 2022). The sensitivity analysis (Figure 6) contradicts ADM1-based studies, in which the rate constants μ_{max} and hydrolysis are generally identified as the most important parameters

(Batstone *et al*., 2002; Galí *et al*., 2009). The preponderance of KI and ΔG_{crit} indicates that ADM1 is not geared toward toxic stress conditions. In comparison, the current structure coincides with the new demands of energised inspired process models (Batstone *et al*., 2015; Adeyemi & Isangadighi, 2025; Kougias & Angelidaki, 2018). Lastly, the enhanced predictive quality of the coupled model (Figure 7) addresses concerns about the model's complexity. Although kinetic-only models are efficient for routine operation, they cannot predict failure under metal strain, which explains the disagreement between model forecasts and observed real-world results reported in previous studies (Chen *et al*., 2014; Ahmadu *et al*., 2019; Zhou *et al*., 2016). The current findings show that thermodynamic feasibility integration is not a choice but a reliable decision-support tool in anaerobic digestion systems that involve metal impacts.

Conclusion

This paper offers a mechanistic enhancement of knowledge of heavy-metal inhibition by explicitly relating kinetic inhibition to thermodynamic feasibility limits in anaerobic digestion systems. Metal-free metallic system underwent analysis in terms of kinetic stability, and a large energetic safety margin, which confirmed that the latter degeneration of performance was a result of inhibitory stress, instead of inherent instability. Heavy metal interventions produced statistically significant effects across all performance indicators, with the largest effect sizes observed for deviations in Gibbs free energy, indicating the central role of energetic limitations in the destabilisation of the processes. Metal-specific studies found significant variation in the degree of inhibition: cadmium and lead caused an earlier energetic collapse than zinc and nickel, thereby resolving anomalies typically observed between empirical IC50 thresholds and immediate digester failure. The findings had a crucial implication: favouring thermodynamic feasibility loss over the total collapse of methane production with progressive metal loading, which characterises energetic collapse as an early-warning mechanism that is not visible in kinetic-only models. Exposure to multiple metals increased the inhibitory effects due to strong synergistic effects, thereby confirming that cumulative toxicity, rather than the concentrations of each metal, determines the actual risk to the digester. The token controls of methane yield, including the $_{crit}$ical Gibbs free energy threshold and the metal inhibition constant, were identified by sensitivity analysis as dominant controls, compared with classical kinetic parameters. The same conclusion was supported by regression analysis, which showed that the effects of total metal burden and energetic deviation are strongly nonlinear, and that disproportionate observations of methane losses are attributable to near-collapse conditions. These complex dynamics were then mapped into operationally relevant states that define the transition between reversible inhibition and irreversible failure via nonlinear threshold behaviour, now known as stability regimes. Lastly, the comparative evaluation demonstrated that the coupled kinetic-thermodynamic model significantly outperformed a kinetic-based model in predicting methane yield and system failure, thereby justifying the increased model complexity. Taken together, these results

indicate that the interaction between microbial growth kinetics and energetic feasibility is a primary determinant of heavy-metal inhibition in anaerobic digestion, and that the systematic underestimation of failure risk results from ignoring thermodynamic constraints. The study thus establishes a more predictive, transferable, and mechanistically underpinned modelling paradigm as a measure and management approach for assessing and managing the stability of the biogas system under metal stress.

Policy- and Practice-Oriented Recommendations

Several policy-influencing recommendations to improve the stability and sustainability of anaerobic digestion systems can be made based on the integrated kinetic-thermodynamic knowledge presented in this paper. One, the regulatory frameworks that guide the acceptance of metal-bearing waste streams should shift their controls from per-metal concentrations to cumulative and synergistic risk levels, particularly for metals that exhibit strong interaction effects, such as cadmium, lead, and copper. Second, larger-scale digester monitoring protocols need to be developed to incorporate indicators of energetic viability, e.g., proxies of Gibbs free energy balance and redox stress, rather than merely surrogates of traditional kinetic or concentration-based metrics. This would enable earlier identification when the process was approaching failure, as thermodynamic collapse has been shown to precede the complete elimination of methane production. Third, the policies should address feedstock management rates based on long-term metal loading rates relative to short-term peaks, given that long-term, chronic loads are irreversible. Fourth, treatment and metal-removal technologies should be applied selectively within strata of metal-specific poisoning of inhibitors and sensitivity, with the most excellent availability of operators, who commit the resources, to the most disruptive contaminants. In modelling and decision support, coupled kinetic-thermodynamic formulations should be adopted in process design, optimization, and control; kinetic-based formulations alone have proven to be significantly underestimates of the likelihood of failure and to exaggerate the system's resilience. The policy implications are that risk-based operational envelopes can be incorporated into permitting and compliance policies for waste-to-energy facilities, particularly in industrial and mixed-waste cases. Finally, any future academic research and clinical interventions should explicitly consider anaerobic digestion as a nonlinear, energy-limiting system, whose stability must be ensured by maintaining reasonable energy margins rather than by apparent tolerance of toxicity thresholds. Suggestions would make biogas production more predictable and reduce spontaneous digester failures; such anaerobic digestion can be more readily developed to support the circular economy and renewable energy in the increasingly complex waste-stream architecture.

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