Supplementary Material

Table S1. Concentration of metallic elements and polyethylene

Element	**Conc. (wt.%)[a]**	**Conc. (wt.%)[b]**
Ga	0.77 ± 0.27	0.7795
In	0.087 ± 0.019	0.0870
Al	5.11 ± 0.59	5.1150
Zn	$2 \times 10^{-5} \pm 1 \times 10^{-6}$	—
Pb	$< 1 \times 10^{-5} \pm 2 \times 10^{-6}$	—
Ag	1.12 ± 0.3	1.1225
Fe	$2 \times 10^{-4} \pm 2 \times 10^{-5}$	0.0002
Ca	0.57 ± 0.025	0.5700
Au	0.012 ± 0.005	0.0120
Cu	0.21 ± 0.087	0.2121
Y	1.87 ± 0.052	1.8753
$\sum$ **Metal**	—	**9.7736**
Polyethylene	—	90.0477
$\sum$**Total**	—	**99.8213**

[a] Average elemental composition in LED matrix in the reference study by Illes et al.
[b] Concentrations in the simulated LED matrix aligning with the reference values by Illes et al.

Table S2. Nutrient media composition

Component	Formula	Concentration (g/L)[a]
D-Glucose	$C_6H_{12}O_6$	30
Sodium nitrate	$NaNO_3$	1.5
Yeast extract	—	1.6
Potassium Phosphate	KH_2PO_4	0.5
Potassium Chloride	KCl	0.025
Magnesium sulfate heptahydrate	$MgSO_4 \cdot 7H_2O$	0.025
Phosphate Buffer Solution		0.1 N
Nutrient pH[a]		5.6 ± 0.2

[a] During Fed-Batch fermentation pH kept at 5.6 ± 0.2 with intermittent NaOH through peristaltic pump automated with pH sensors. In bioleaching trials, pH of supernatants as well as control solutions were adjusted to 3 ± 0.2 using 1N HNO_3.

Table S3. Bioleaching Experimental Design Overview

Category	Parameters	Description
Lixiviant	Supernatant	Fermentation liquid taken from Fed-Batch fermentation by *Aspergillus Niger (ATCC1015)* at 384 h
	Abiotic Control	Synthetic control solution consisting of nutrient media and chemical organic acids aligning with the composition of the supernatant solution.
	Blind Control	Nutrient media used in fed-batch fermentation (See Table S2)
Waste Materials	LED Matrix	Simulated waste matrix consisting of LED components
	Gallium waste	Analytical grade Ga_2O_3
pH	Fermentation media	pH 5.6 ± 0.2
	Leaching Environment	pH 3.0 ± 0.2 (adjusted via 1N HNO_3).
Sampling and Experimental Validation	Sampling Points	Prior to trials and after adding the waste materials (t=0), and at t = 5, 10, 15, 24 hours.
	Reproducibility	Triplicate experiments (#1, #2, #3).

Table S4. Initial Gallium (Ga) content in solid waste materials determined by total digestion.

Waste Matrix	[$Ga_{initial}$ ($mg \cdot kg^{-1}$)[a]
LED Waste	6650 ± 70.71
Ga_2O_3	7439 ± 5.3

[a] Concentration of Ga in waste materials was determined by ICP-MS following acid digestion (Supranur 69%).
* $\pm$ Standard deviations (STD) represent variations across representative samplings ($n = 3$) in waste materials.

Table S5. Dissociation constants and fractions of organic acids present in the supernatant solution

Compound	Molecular Formula	pK_a (25°C)	f_H [a]	f_H (pH =3)
Oxalic Acid	$C_2H_2O_4$	$pK_{a1} = 1.25$ $pK_{a2} = 4.27$	$f_{H1} = 0.39$ $f_{H2} = 6 \times 10^{-4}$	$f_{H1} = 0.98$ $f_{H2} = 0.43$
Citric Acid	$C_6H_8O_7$	$pK_{a1} = 3.13$ $pK_{a2} = 4.76$ $pK_{a3} = 6.40$	$f_{H1} = 0.12$ $f_{H2} = 3.3 \times 10^{-3}$ $f_{H3} = 1 \times 10^{-4}$	$f_{H1} = 0.43$ $f_{H2} = 0.0171$ $f_{H3} = 4 \times 10^{-4}$
Gluconic Acid	$C_6H_{12}O_7$	$pK_a = 3.86$	$f_{H1} = 0.0366$	$f_{H1} = 0.2$

[a] Represents the dissociated fraction (f_H) aligning with supernatant solution: *Oxalate (226 mM, pH 1.05), Citrate (42.7 mM, pH 2.28), and Gluconate (179.5 mM, pH 2.18).*

Table S6. ICP-MS analysis of Gallium (Ga) concentrations at t = 0 h and t = 24 h

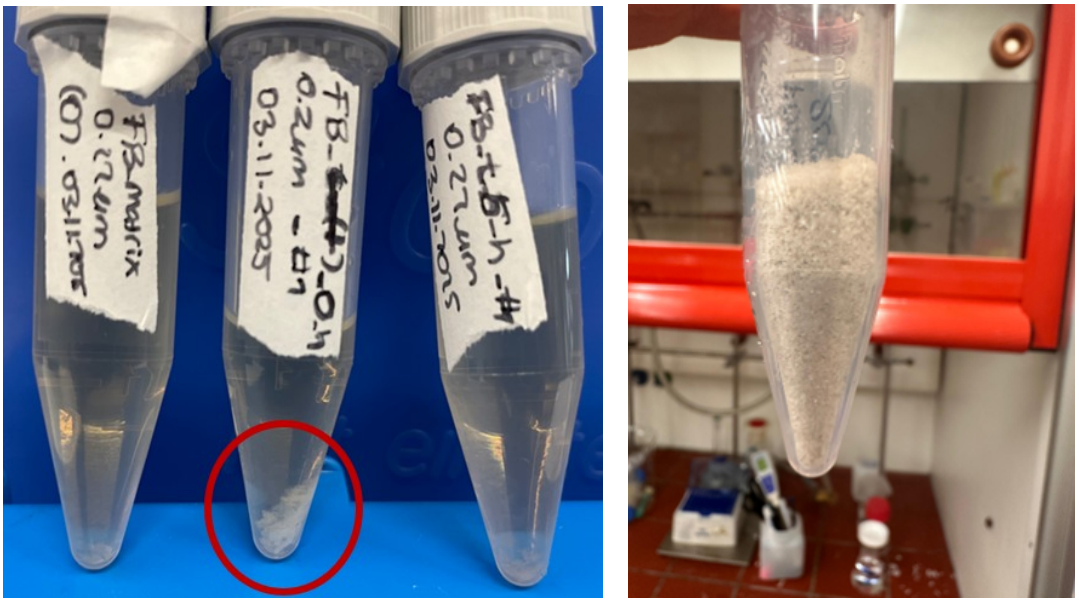
Sample Matrix[a]	Ga ($\mu g \cdot L^{-1} \pm$ STD[c])[b]$_{(t = 0\ h)}$	Ga ($\mu g \cdot L^{-1} \pm$ STD[c])$_{(t = 24\ h)}$
BX	< 5	< 5
CX	31.33 ± 6.66	6300 ± 624.5
SX	80 ± 56.04	12933.33 ± 368.9

[a] BX: Blind Control; CX: Abiotic Control; SX: Supernatant.
[b] Measured Ga concentrations ($\mu g \cdot L^{-1} \pm$ STD at t = 0, after adding the waste material to the leaching matrix.
[c] Standard deviations (STD) represent the experimental variability across reproducibility studies ($n = 3$).

Table S7. Oxalic acid (OA) concentration profile across experimental matrices and time intervals.

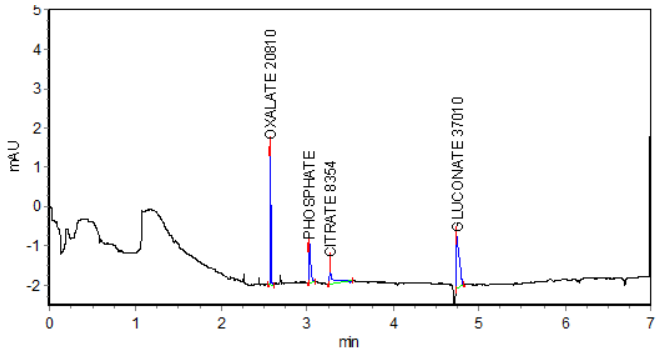
Sample Matrix	OA Concentration ($g \cdot L^{-1}$) ± SD	
	$t = 0$ h[a]	$t = 24$ h[b]
BX[c]	n.d.	n.d.
CX	20.36 ± 1.48	20.56 ± 3.20
SX[d]	9.27 ± 0.81	13.30 ± 0.29
$t = 5\ h$	10.80 ± 3.01[e]	
$t = 15\ h$	14.087 ± 2.23[e]	

[a] Initial concentrations measured immediately following waste material addition.
[b] Final concentrations at the conclusion of the 24-hour leaching trial.
[c] n.d.: Not detected; Capillary Electrophoresis (CE) yielded no signal for organic acids.
[d] Post-fermentation stock concentration (stored at 4 °C) was 20.36 ± 0.40 $g \cdot L^{-1}$.
[e] Intermediate kinetic values measured specifically for the bioleaching matrix (SX).

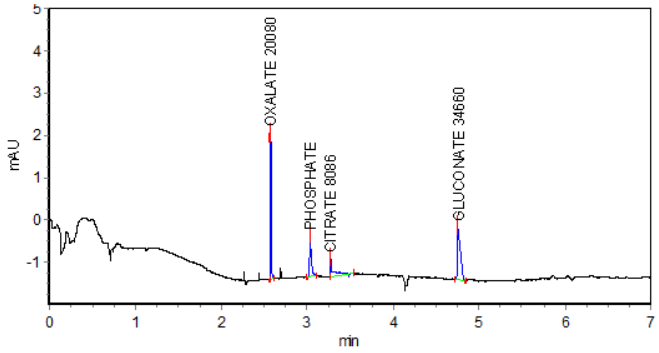


(a) **(b)**

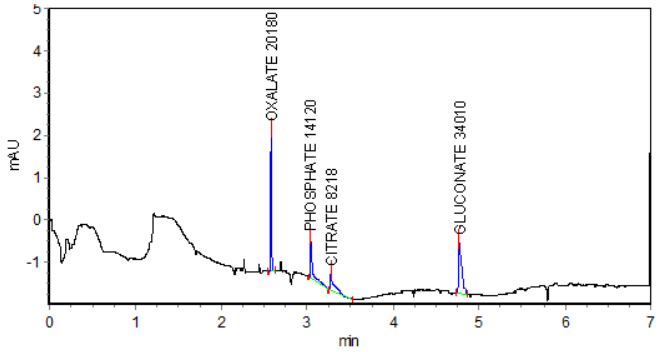
Figure S1. a. Precipitation observation in supernatant solution prior to bioleaching experiments in sampling vials;
b. Unknown washed and dried precipitate separated from the supernatant solution6



(a) Electropherogram of initial fermentation supernatant.

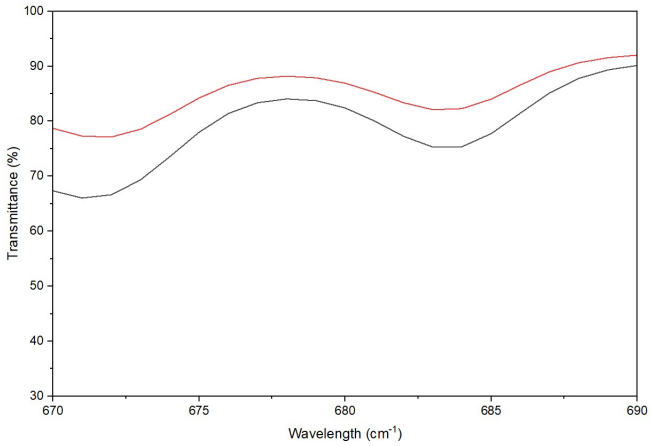


(b) Comparison of organic acid profiles during leaching.

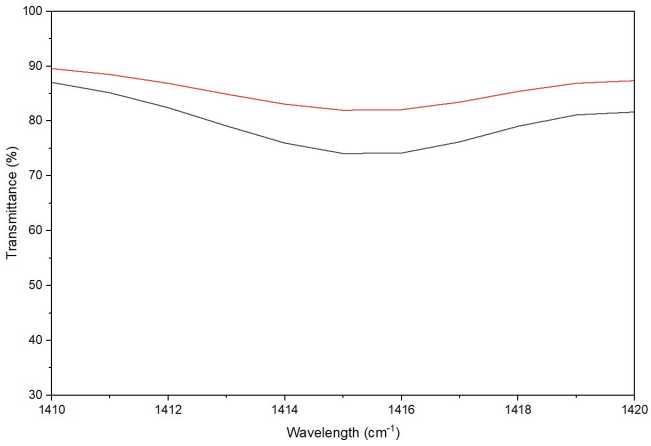


(c) Final residue analysis and acid consumption.

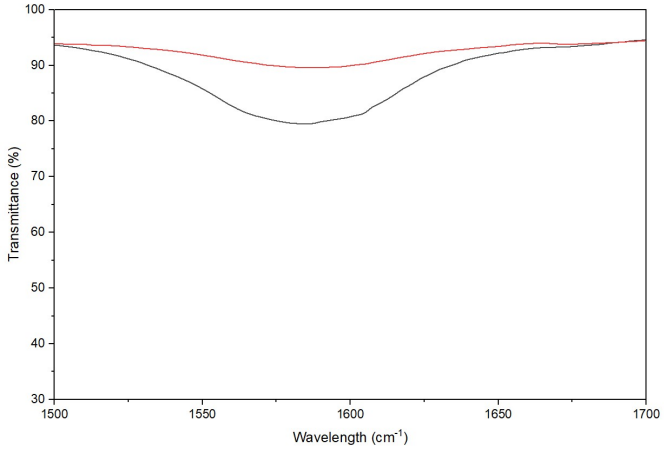
Figure S2. Capillary Electrophoresis (CE) spectra analyzing organic acid concentrations in specific peaks correspond to oxalic, citric, and gluconic acids. External calibration was applied in *ELFORUN* simulation for the quantification



(a) Region I: 670–685 cm^{-1}



(b) Region II: 1410–1420 cm^{-1}



(c) Region III: 1550–1700 cm^{-1}

Figure S3. FTIR spectral analysis of residues: LED raw material (gray line) and Supernatant (red line).

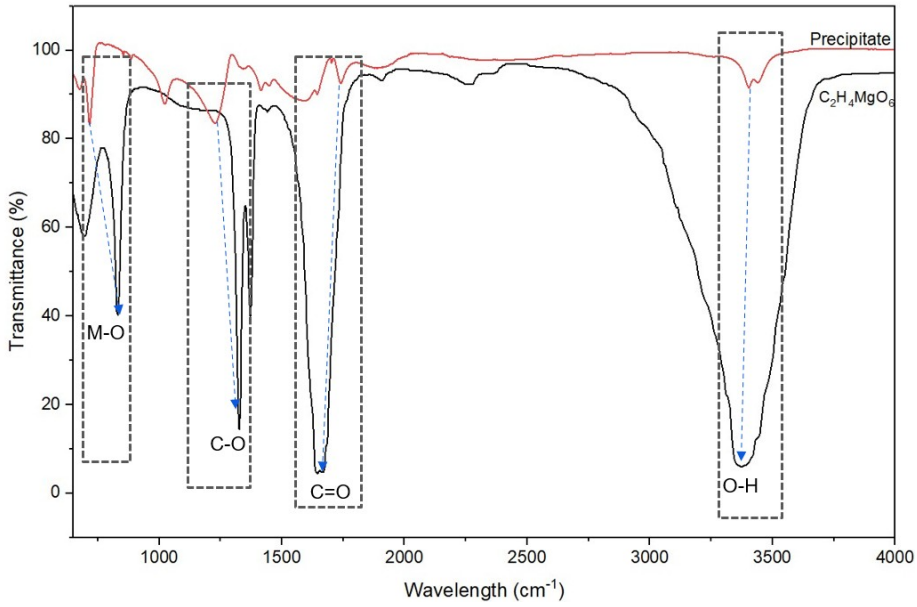
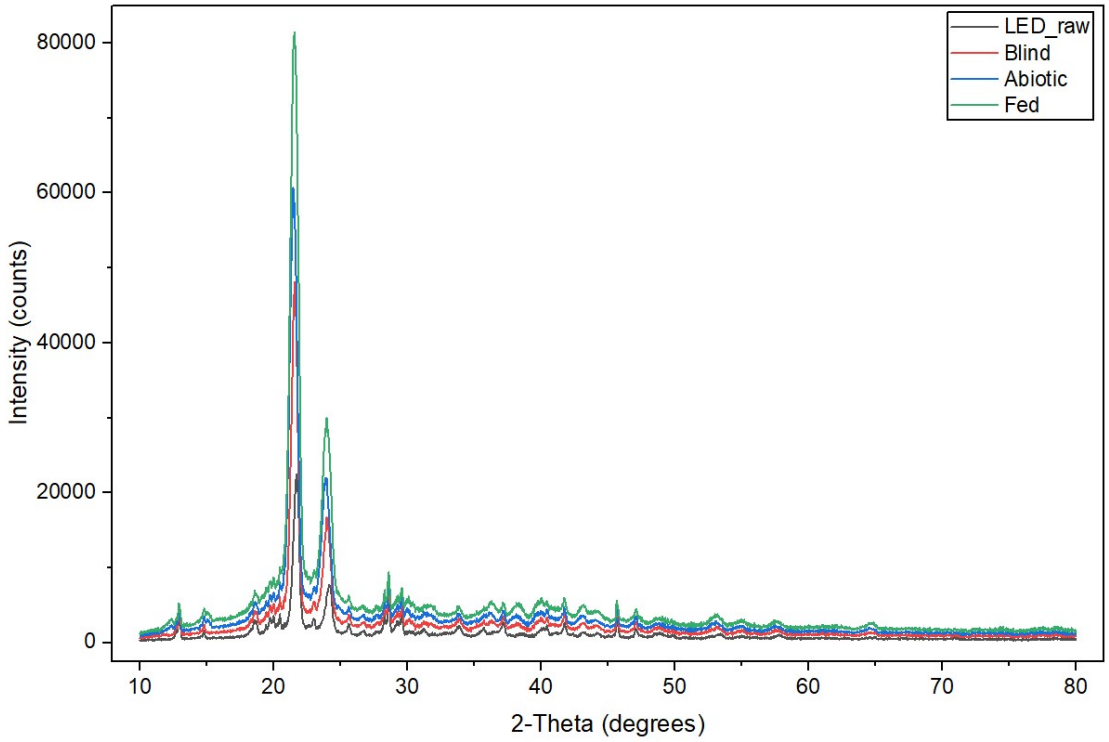
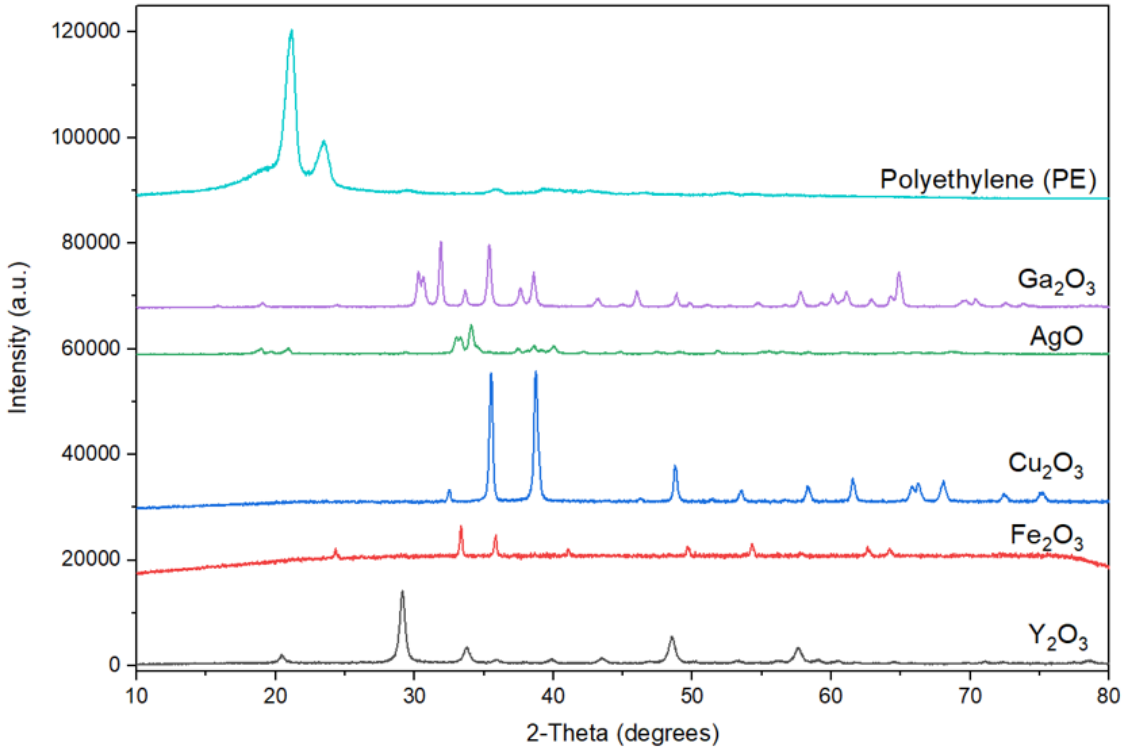


Figure S4. FTIR spectral analysis of unknown oxalate crystal and identified peak belonging to magnesium oxalate (NIST database)



(a) Experimental XRD patterns of bio-leached residues.



(b) Reference XRD patterns for standard oxides, and polyethylene (PE).

Figure S5. Comparative XRD analysis of residues: LED raw material (gray),Supernatant control (red), and Supernatant (blue) compared against standard oxide references.

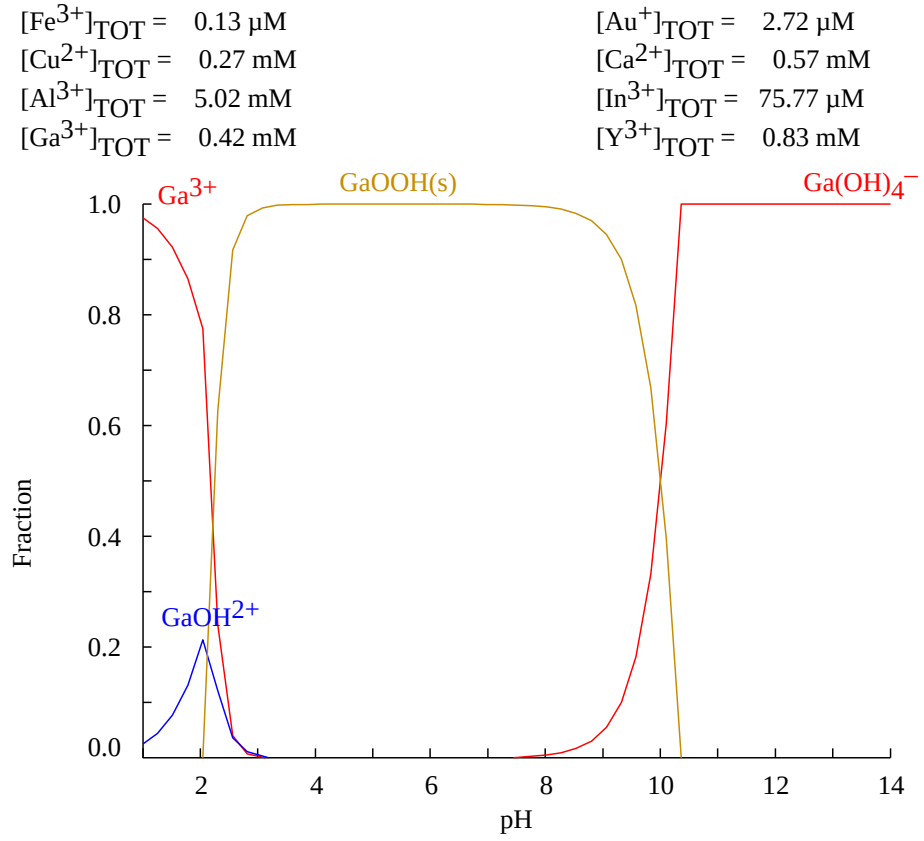


Figure S6. Gallium (Ga) speciation in the presence of interfering ions in LED matrix

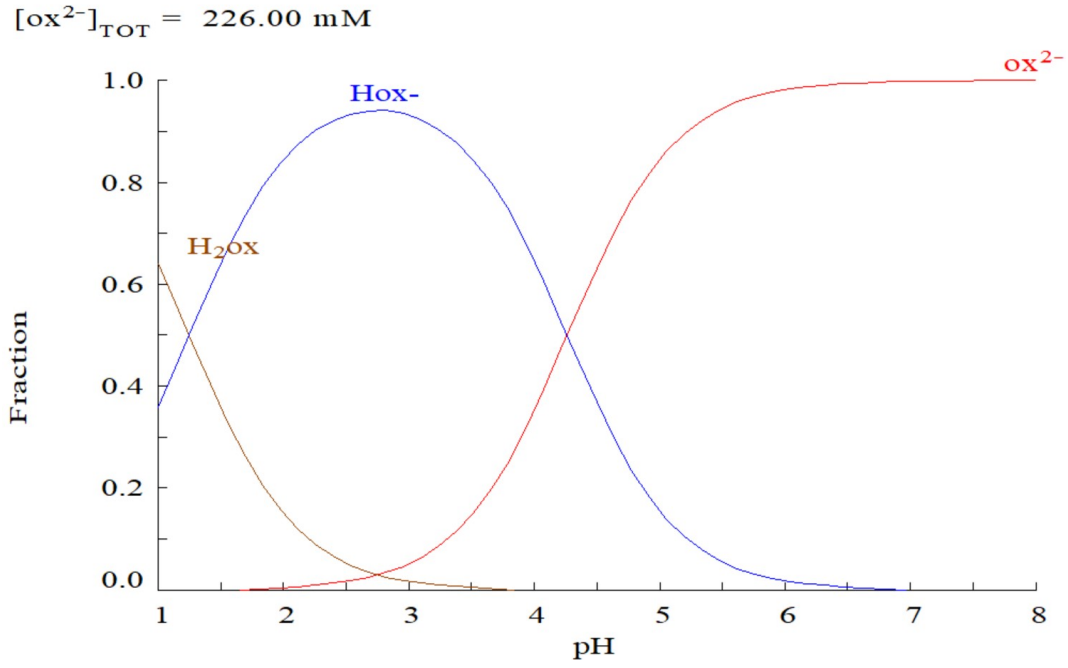


Figure S7. Oxalate speciation under varying pH

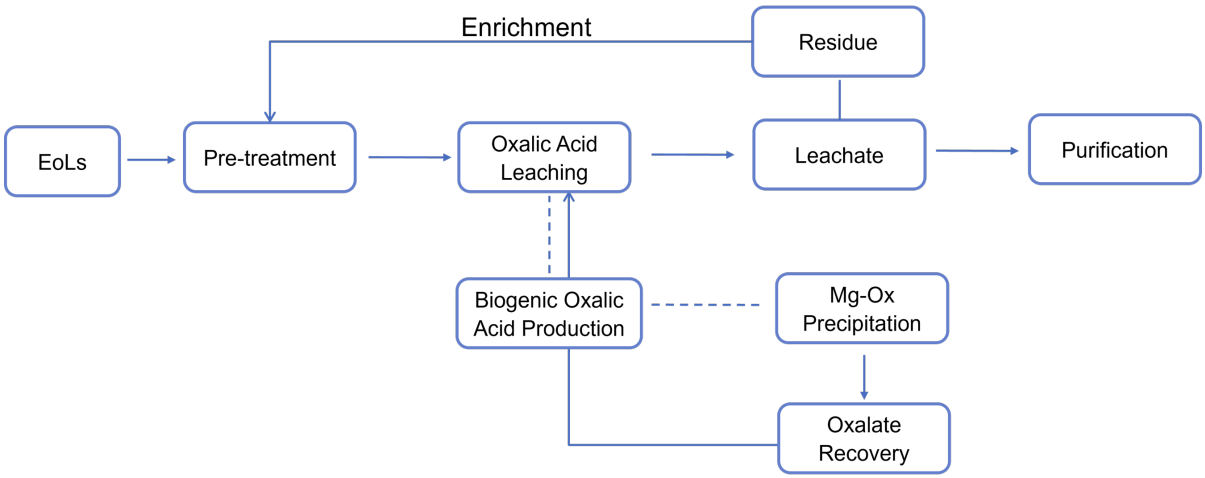

Enrichment
Residue
EoLs
Pre-treatment
Oxalic Acid Leaching
Leachate
Purification
Biogenic Oxalic Acid Production
Mg-Ox Precipitation
Oxalate Recovery

Figure S8