

Supporting information for:

Precipitation of vanadium from leachate solutions by reduction with hydrazine

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1 Appearance of colloidal suspension at different pH values

Sulfuric acid was added to a solution of the nano-colloid formed from reduction of a pure V^{5+} solution. Observations were recorded at each measured pH.

Table S1. Observations when adding sulfuric acid to the black nano-colloid.

pH	Observation
3.56	Dark blue/green transparent solution
5.58	Dark solution with black precipitate
6.50	Dark solution with black precipitate
7.64	Dark solution with black precipitate
8.66	Dark solution with black precipitate
9.65	Initial agglomerated solution

2 Zeta potential measurement

Distilled water was filtered twice through a 0.45 μm nylon membrane. This twice filtered distilled water was used as the dispersant for the zeta potential measurement.

	Mean (mV)	Area (%)	St Dev (mV)
Zeta Potential (mV): -14.0	Peak 1: -14.0	100.0	7.49
Zeta Deviation (mV): 7.49	Peak 2: 0.00	0.0	0.00
Conductivity (mS/cm): 0.564	Peak 3: 0.00	0.0	0.00

Result quality Good

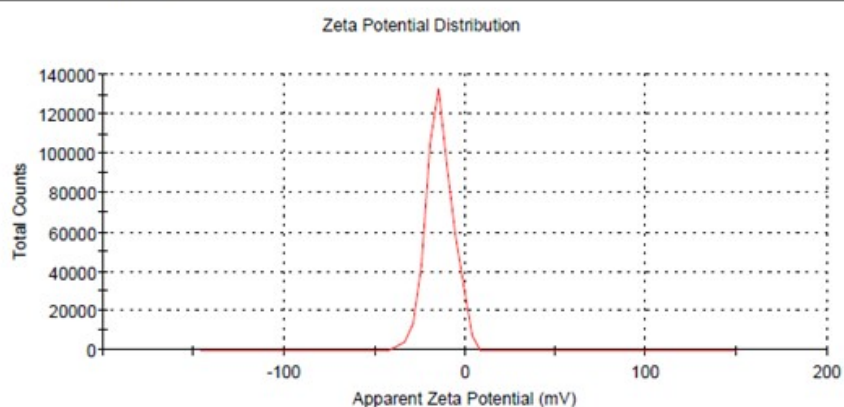


Figure S1. Zeta potential measurement of the black nano-colloidal solution obtained after reduction of AC leachate with hydrazine.

3 Particle size analysis of samples

Distilled water was filtered twice through a 0.45 μm nylon membrane. This twice filtered distilled water was used as the dispersant for the particle size analyses.

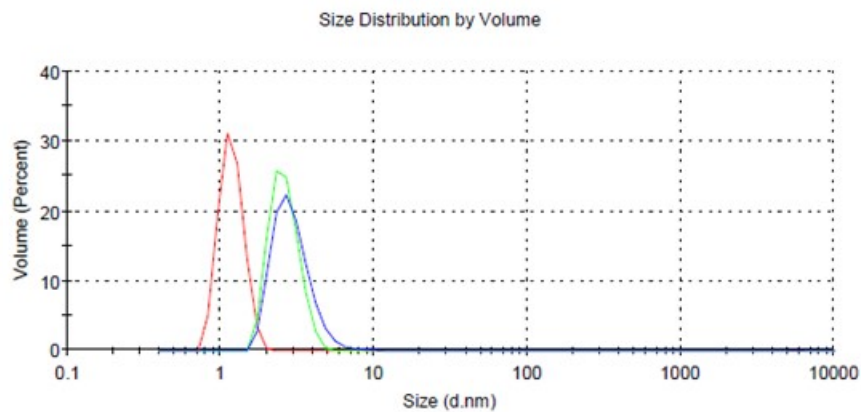


Figure S2. Particle size measurements (3 replicates, volume distribution) of the black solution obtained after reduction of AC leachate.

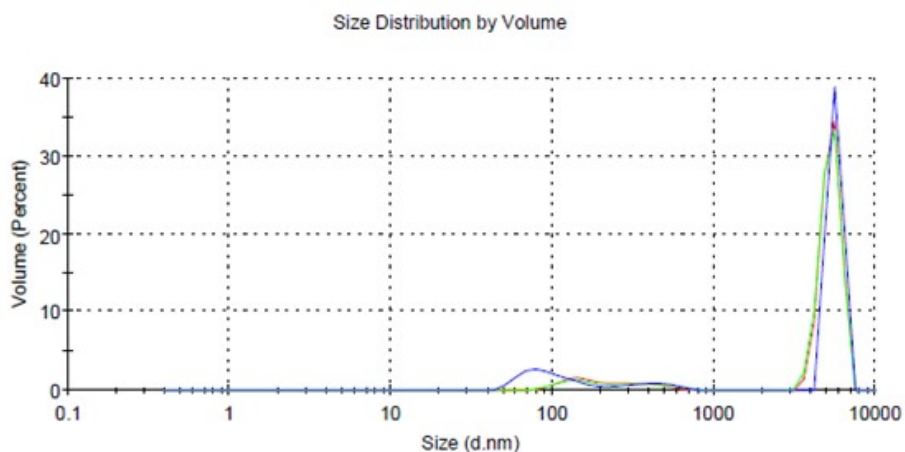


Figure S3. Particle size measurements (3 replicates, volume distribution) of the agglomerated black solution obtained after reduction of AC leachate.

4 Ripening of nano-colloidal solution using a flocculant

Flocculant PK 311 (1 g) was added to distilled water (1 L) and stirred vigorously overnight at RT. A small amount of the stock flocculant solution (0.1 mL) was added to reduced AC leachate (50 mL) and stirred for 5 minutes before being allowed to sit for 10 minutes. After this time, a sample of this solution was taken and analysed.

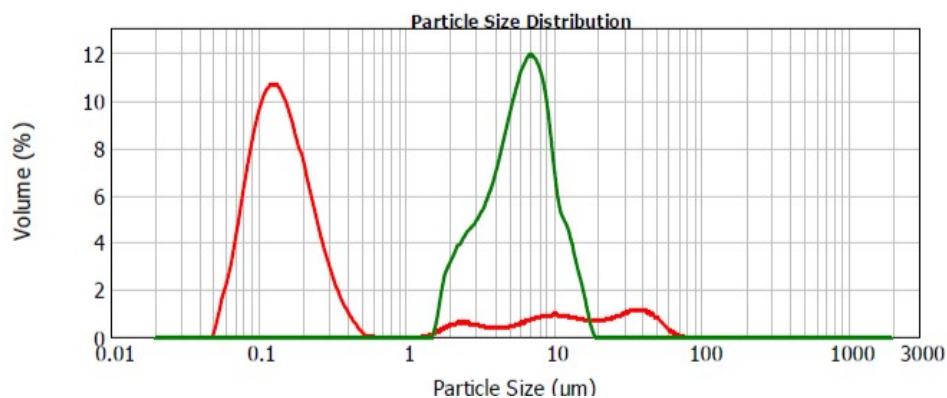


Figure S4. Particle size distribution of the initial black colloidal solution (red curve), and the black solution after the addition of the flocculant PK 311 (green curve).

5 Relationship between initial leachate parameters and precipitation efficiency

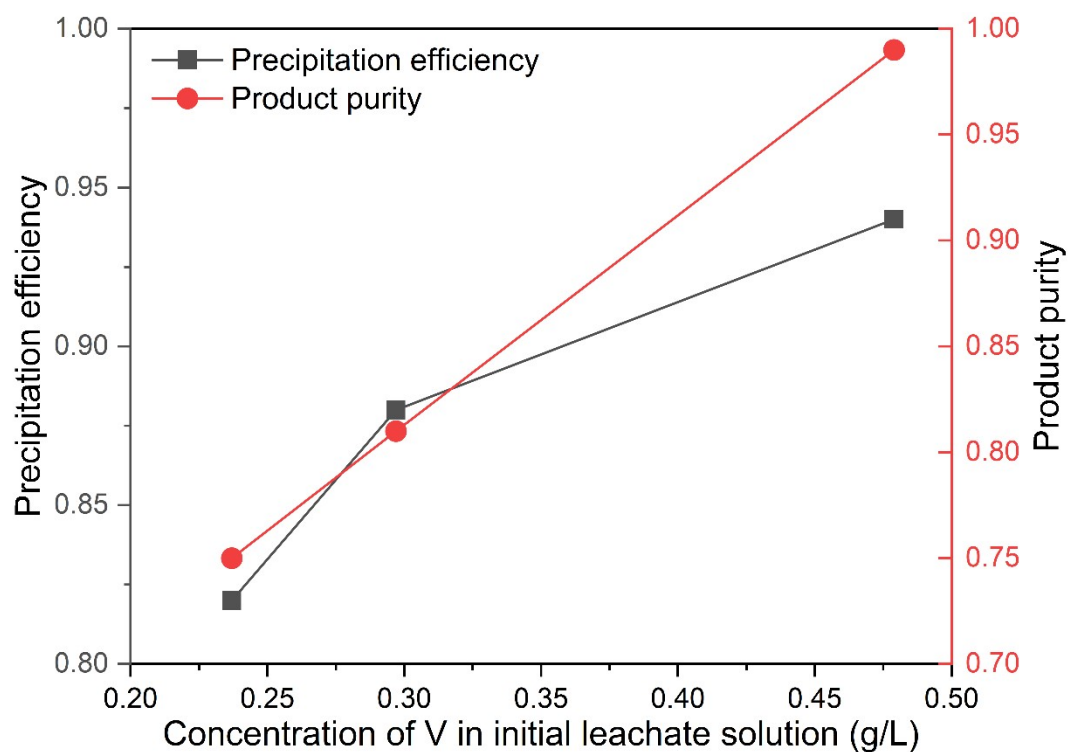


Figure S5. Plot showing the relationship between the concentration of vanadium in the initial leachate solution, and the precipitation efficiency and product purity achieved.

6 Additional TEM images

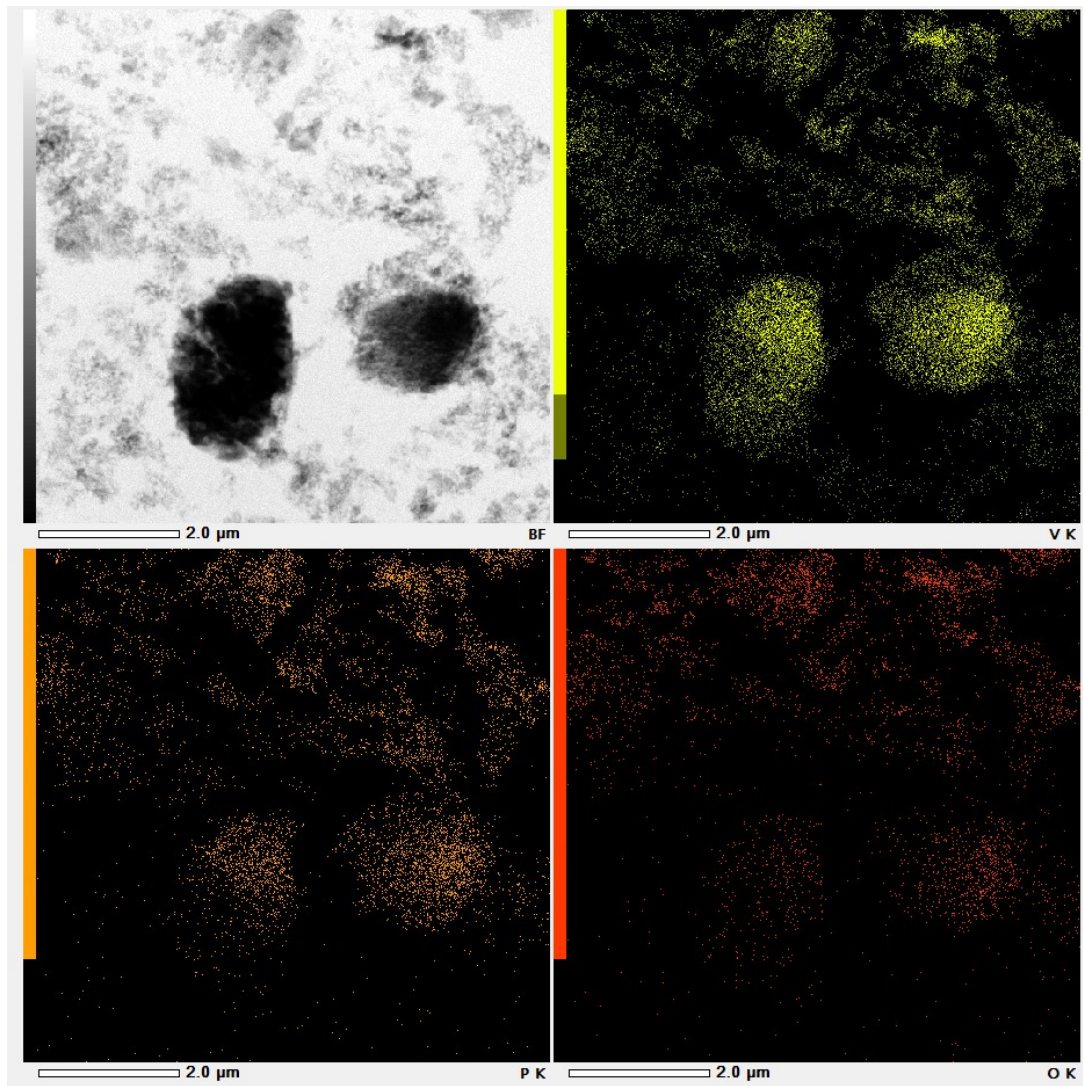


Figure S6. TEM/EDS map (20k magnification) of agglomerated nanoparticles from AC leachate reduction. Top left: bright field image of the black precipitate, top right: vanadium distribution, bottom left: phosphorus distribution, bottom right: oxygen distribution.

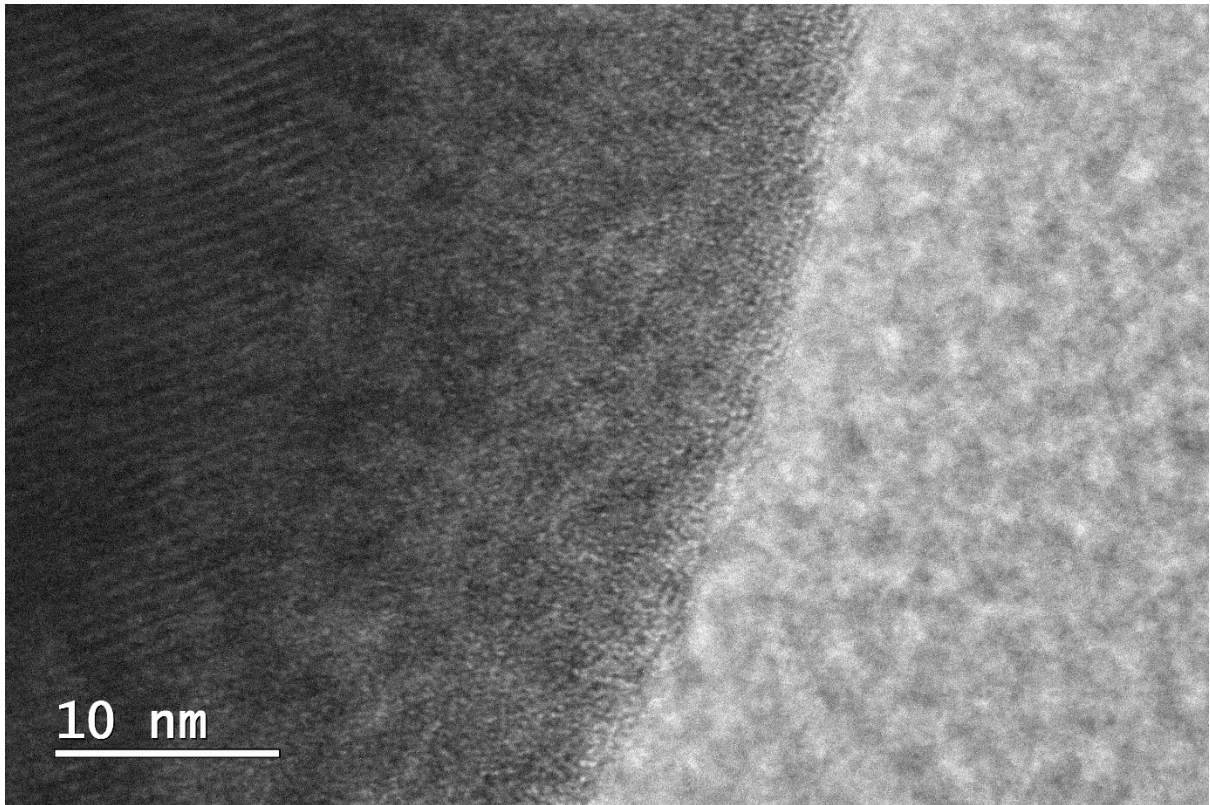


Figure S7. TEM image of agglomerated cylindrical nanorods from pure V^{5+} solution post-agglomeration (500k magnification).

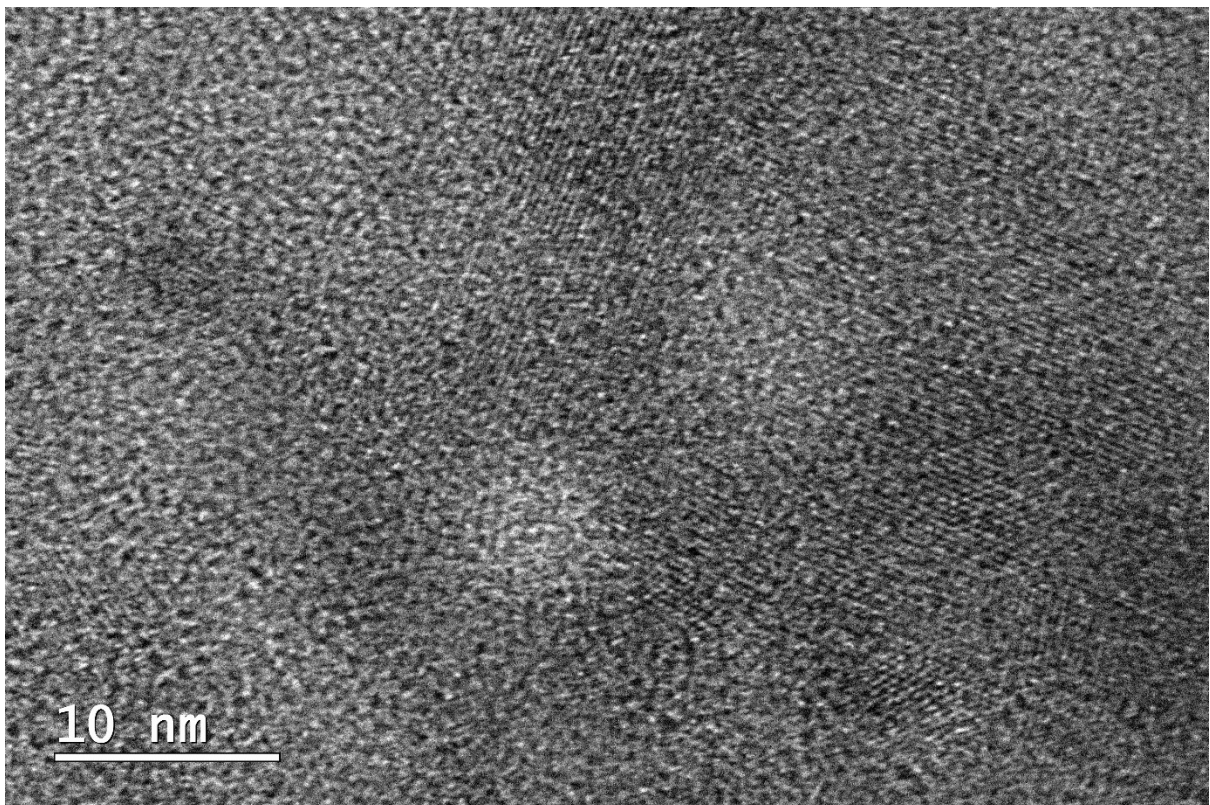


Figure S8. Pre-agglomeration nanoparticles from AC leachate reduction (500k magnification).

7 “Green Chemistry” metrics calculations

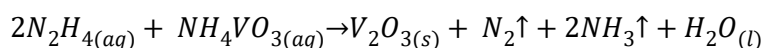
E-factor calculations

The *E-factor* describes the environmental acceptability of a process through comparison of the mass of waste generated with the mass of product formed in the process. The *E-factor* is defined as follows:

$$E \text{ factor} = \frac{m_{\text{waste}}}{m_{\text{product}}}$$

Where m_{waste} is defined as the total mass of the process waste, and m_{product} is defined as the total mass of the process product. The *E-factor* of the hydrazine precipitation step was calculated and compared to the conventional ammonium-salt precipitation route.

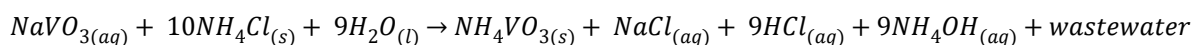
The precipitation method with hydrazine proposed here allows for the formation of solid V_2O_3 , H_2O , and N_2 and NH_3 as gases that can be recaptured and recycled back into the process:



As this process leaves behind clean water and gases that can be recaptured and recycled, $m_{\text{waste}} = 0$, therefore:

$$E \text{ factor} = \frac{0}{m_{\text{product}}} = 0$$

By contrast, the conventional ammonium-salt precipitation route typically involves the addition of a large excess of ammonium chloride (2-10 equivalents) to a sodium vanadate solution while heating. This gives ammonium vanadate as a product, while generating contaminated wastewater as a byproduct.



The parameters used for the calculation of the *E-factor* for the ammonium chloride precipitation process are shown in tables S2 and S3 below. A theoretical V solution concentration of 1000 ppm was assumed, with contaminated, unrecyclable wastewater included in the waste mass calculation. Literature examples give the excess of ammonium chloride required as between 2 and 10 equivalents, resulting in the *E-factor* here being calculated as a range.^{1,2}

Table S2. Lower bound parameters for E-factor calculations for ammonium chloride precipitation.

	Reagents		Products				
	NaVO ₃	NH ₄ Cl	NH ₄ VO ₃	NH ₃	HCl*	NaCl*	Wastewater*
Molar Equivalents	1	2	1	1	1	1	
Mol/t	19.63	39.26	19.63	19.63	19.63	19.63	
Molar mass (g/mol)	121.93	53.49	116.98	17.03	36.46	58.44	
Mass (kg/t leachate)	2.39	2.10	2.30	0.33	0.72	1.15	1000000

*Products are considered to be waste for calculations as regeneration is cost prohibitive and usually not done.

Table S3. Upper bound parameters for E-factor calculations for ammonium chloride precipitation.

	Reagents		Products				
	NaVO ₃	NH ₄ Cl	NH ₄ VO ₃	NH ₃	HCl*	NaCl*	Wastewater*
Molar Equivalents	1	10	1	9	9	1	
Mol/t	19.63		19.63	176.67	176.67	19.63	
Molar mass (g/mol)	121.93		116.98	17.03	36.46	58.44	
Mass (kg/t leachate)	2.39		2.30	3008.92	6441.51	1.15	1000000

*Products are considered to be waste for calculations as regeneration is cost prohibitive and usually not done.

Using these parameters results in the following *E-factor* calculations for the lower and upper bounds:

$$E \text{ Factor} = \frac{1.007589}{0.002293} = 436.3$$

$$E \text{ Factor} = \frac{1.007589}{0.002296} = 438.8$$

Atom economy calculations

Atom economy is a measure of the chemical efficiency of a process, whereby the proportion of atoms from the starting mixture that are incorporated into the final product are calculated. *Atom economy* is expressed as below:

$$\%AE = \frac{M_{product}}{M_{total}} \times 100$$

Where $M_{product}$ is the molar mass of the product, and M_{total} is the sum of the molar masses of all reagents. The parameters used for the atom economy calculations and the atom economies of the proposed hydrazine precipitation pathway and the conventional ammonium-salt precipitation process are shown in table S4.

Table S4. Atom economy calculations for the discussed precipitation pathways.

Process	$m_{product}$	m_{total}	%AE
Ammonium chloride precipitation (lower equivalent)	116.98	228.91	51%
Ammonium chloride precipitation (higher equivalent)	116.98	656.84	18%
Hydrazine precipitation (lower equivalent)	149.03	82.94	56%
Hydrazine precipitation (higher equivalent)	149.88	266.01	56%

Reaction mass efficiency calculations

Reaction mass efficiency is a measure of how efficiently the reaction has converted starting materials into product, taking into account both atom economy and percentage yield of the process. Reaction mass efficiency values for the conventional ammonium-salt precipitation process and the proposed hydrazine precipitation are presented in table S5 below, along with a summary comparison of the two processes.

Table S5. Summary comparison of green metric calculations between the conventional ammonium-salt pathway and the reductive hydrazine pathway.

Parameter	Conventional ammonium-salt precipitation	Reductive hydrazine precipitation
Reagent consumption	2-10 molar equivalents	1.5 molar equivalents
Precipitation efficiency	99%	82-94%
Product purity	98-99%	75-99%
Recyclable wastewater	No	Yes
E-factor	436-439	0
Atom economy	18-51%	56%
Reaction mass efficiency	17-51%	46-52%

8 References

1. P. Xiong, Y. Zhang, S. Bao and J. Huang, *Hydrometallurgy*, 2018, **180**, 113-120.
2. G. Lin, J. Huang, Y. Zhang and P. Hu, *Materials*, 2022, **15**, 1945-1959.