E-ISSN: 2709-9423
P-ISSN: 2709-9415
Impact Factor (RJIF): 5.29
JRC 2025; 6(2): 147-156

www.chemistryjournal.net
Received: 27-07-2025
Accepted: 28-08-2025

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Green perspectives on sulphur chemistry: Sustainable pathways in organic synthesis

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Abstract
Sulphur chemistry is one of the core of sustainable organic synthesis where molecular innovation and environmental responsibility is linked. In the past sulphur based transformations involved the reliance on toxic reagents, dangerous waste streams and energy-demanding processes. Nevertheless, the alternative developments put in existence as of late owing to the guidelines of green chemistry have changed these operations giving selective, efficient as well as environmentally aware pathways. The combination of renewable energy systems, recyclable catalysts and benign solvents has reversed classical reactions to the following, sulfonation, thiolation and oxidation. New approaches, including photocatalytic activation and electrochemical activation, allow using high-yield sulphur conversions at ambient conditions, and bio-based alternatives can be developed, namely the thiolation via biocatalytic means in aqueous solutions. The paper will explore the history of green sulphur chemistry by the innovative catalyst, intensifying the process, and its integration in the circular economy. It has quantitative measures such as E-factor, atom economy, and life-cycle assessment (LCA), which compare the conventional and sustainable methods. Implementation of artificial intelligence (AI), digital twins, and renewable sources are a step to a system of autonomous and zero-waste production of sulphur. Given the convergence of catalysis, biotechnology and data science, green sulphur chemistry is a redefining approach that has the potential of attaining environmental sustainability in the worldwide chemical sector.

Keywords: Sulphur chemistry, green chemistry, catalysis, photocatalysis, electrocatalysis, biocatalysis, circular economy, sustainability, life-cycle assessment

1. Introduction
1.1 The Role of Sulphur in Modern Chemistry
Organic synthesis has always been heavily based on sulphur chemistry, as it demonstrates multiple oxidation states (-2 to +6), redox flexibility through a wide variety of bonding patterns, and thereby represents numerous transformations. This ability to be versatile gives sulphur atoms the capacity to be core functional units as used in pharmaceuticals, agrochemicals, dyes, and functional materials. One-third of marketed drugs, at least, include at least one sulphur atom, which indicates its pharmacological importance. These are penicillins, sulfonamides, and omeprazole, and the biological action of each of them involves unique functional groups of sulphur (Tripathi *et al*., 2020) [41].
Outside the pharmaceutical, materials and industrial use of sulphur include vulcanization of rubber, petroleum refining catalysts, and new battery technology (Zhang and Zhao, 2018) [42]. However, the classical sulphur based reactions are still related to a range of serious environmental and safety issues.

1.2 Environmental and Industrial Challenges
The application of sulphur in the past has been based on sodium corrosive sulfurous acid, sulfur dioxide, and sulfurous acid (Anastas and Warner, 2000) [43]. The reagents come with toxic byproducts, substantial amounts of sulphate byproducts and volatile organic emissions. As an example, the sulfonation of chlorosulfonic acid has a low atom economy and large effluent, which is to be neutralized (Sheldon, 2018) [44]. The cumulative impact is a contributor of air pollution, acidity as well as inefficiency of energy use. Moreover, the classical solvents (such as dichloromethane or toluene) have high global warming potential (Capello *et al*., 2007) [3], which only enhances the intensity of carbon in sulphur chemistry.

1.3 Emergence of Green Chemistry Principles
Anastas and Warner (2000) [43], with the introduction of the 12 Principles of Green Chemistry, made a paradigm shift in the manner in which waste management was done in a way that prevented pollution at the molecular design phase. The focus of these principles is atom economy, less harmful solvents, renewable feedstocks and energy efficiency. In the context of sulphur chemistry, they promote the substitution of stoichiometric reagents by catalytic systems as well as fossil-based solvents by aqueous or bio-based solvents (Sheldon, 2018) [44].
The green sulphur chemistry breakthrough was the solvent-free thiol-ene equivalent of a click reaction, which is characterized by almost 100% atom economy and an insignificant amount of waste (Hoyle and Bowman, 2010) [6]. These phases combined with photocatalytic and biocatalytic systems are an illustration of marrying sustainability and performance.

2. Methodological Framework for Sustainable Sulphur Chemistry
2.1 Green Synthetic Design
To shift towards the process of sustainable synthesis, a complete redesign is needed with the focus on efficiency, specificity, and reproducibility. The modern green sulphur chemistry is based on the three strategic pillars:
1. Substitution of the harmful reagents with innocuous ones.
2. Activation Nonthermal activation (microwave, ultrasound, light).
3. Process intensification and catalyst Recalculability with heterogeneous and biocatalytic systems.

These pillars together balance the sulphur production process with ethical and environmental directives of the green chemistry (Anastas and Zimmerman, 2018) [45].

Table 1: Comparative Overview of Traditional vs. Green Sulphur Methodologies

Aspect	Traditional Sulphur Process	Green Sulphur Alternative
Solvent	Dichloromethane, toluene	Water, ethanol, ionic liquids
Catalyst	Stoichiometric acids (H_2SO_4, $SOCl_2$)	Recyclable metal or enzyme catalysts
Energy Input	Thermal (>120°C)	Photocatalytic or microwave-assisted (<50°C)
Waste Generation	High sulphate residues	Recyclable or minimal waste
Atom Economy	40-60%	80-100%
Toxicity	High	Low to negligible
E-Factor	40-50	<10

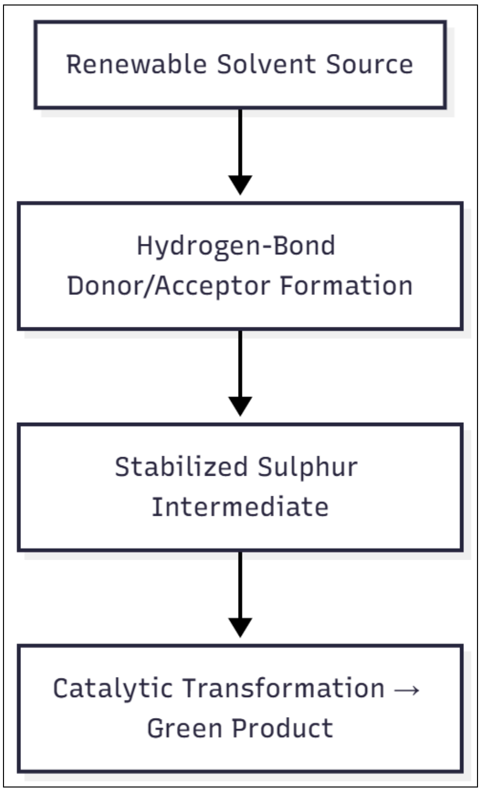

Fig 1: Conceptual Framework of Green Solvent Application

2.2 Green Solvents and Media
Most of the wastes in chemical processes are solvents. Using alternative solvents that are greener, namely water, ethanol, glycerol, ionic liquids (ILs), or deep eutectic solvents (DES), is of high importance in order to have a smaller environmental footprint (Clarke *et al*., 2018) [2]. Stabilized reactive intermediates through hydrogen-Bond interactions (e.g., choline chloride and urea) allow the catalyst to retain the activity of the catalyst (Zhao *et al*., 2021) [30].
Supercritical CO 2 (scCO 2) is also a non-toxic and recyclable oxidation and coupling reaction medium with a facile separation and none of the residual solvent wastage The solvent systems improve the safety of the processes as well as align with low-emission industrialization objectives.

2.3 Catalytic Pathways
2.3.1 Heterogeneous Catalysis
Solvents Pd/C heterogeneous catalysts (usually combined with other metals, such as CuO-TiO 2 or MoS 2), aqueous C-S coupling reactions have also enjoyed considerable success to date (Huang *et al*., 2022) [7]. As an example, Pd/C allows the conjugation of thiols and aryl halides in ethanol-water solutions with over 95% of the yield and minimum leaching (Li *et al*., 2020) [40]. These systems are scalable and have a a number of catalytic cycles which can be recycled.

Table 2: Catalytic Methodologies for Green Sulphur Transformations

Catalytic Type	Typical Catalyst	Reaction Example	Green Advantage
Heterogeneous	Pd/C, CuO-TiO_2	Thiolation, sulfonation	Recyclable, solvent-free
Biocatalytic	Sulfur transferase, desulfurase	C-S bond formation	Mild, aqueous medium
Photocatalytic	g-C_3N_4, MoS_2	Sulfoxidation	Light-driven, low energy
Electrocatalytic	Ni electrodes	Aryl sulfonation	Reagent-free oxidation

2.3.2 Biocatalysis
The enzymes, used in biocatalytic systems, include the sulfurtransferases and cysteine desulfurases to catalyze the thiolation and oxidation under the mild aqueous conditions

(Wong *et al*., 2022) [46]. The fixation of enzymes on polymeric supports enhances re-use and facilitates operations through continuous-flow. These enzymatic systems reduce byproducts, do not need an added oxidant and provide a high degree of regioselectivity.

2.3.3 Photocatalysis and Electrocatalysis

Photocatalytic systems that employ g-C 3 N 4 and TiO2 use visible light as an oxidative transformer (Xie *et al*., 2021) [47]. Equally, methoxyl Charleston electric An electrochemical sulfonation process where nickel or graphite electrodes are used replaces chemical oxidants with electric current, and faradaic yield is greater than 90 percent (Tay *et al*., 2022) [48]. These electrocatalytic processes are almost carbon-neutral in the case of renewable energy as the source.

2.4 Energy-Efficient Methods

Process intensification with microwave and ultrasonic assistance is also dramatic, causing reaction times to decrease significantly and energy consumption to go down (Jiménez-Gonzalez *et al*., 2011) [5]. Solvents are avoided in the synthesis of C47-S bonds by mechanism chemical milling and the yields are high even at ambient temperature (Hernández *et al*., 2017) [32]. These procedures improve throughput whilst ensuring the performance of green measures.

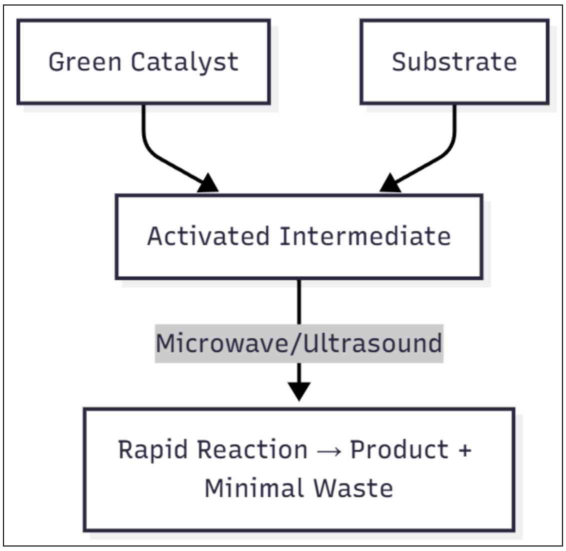

Fig 2: Energy-Efficient Sulphur Transformation

3. Results and Discussion

3.1 Sustainable Feedstocks and Circular Resource Use

High volume, renewable feedstock Elemental sulphur obtained by processing petroleum desulfurization is a promising feedstock. Inverse vulcanization is a reaction of elemental sulphur with unsaturated organic monomers to create crosslinked polysulfide polymers, which are applicable in optics, batteries and agriculture (Lim *et al*., 2019) [49]. This valorization will create a waste material that can be used in the creation of sustainable material which aligns with the principles of a circular economy.

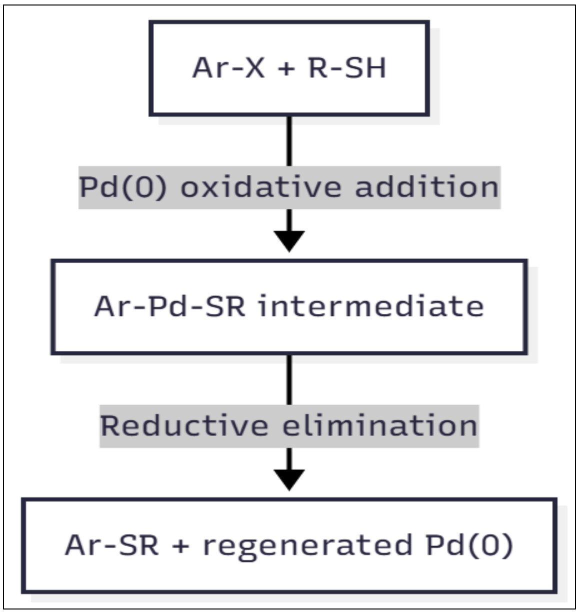

Fig 3: Mechanistic Pathway for Pd-Catalyzed Thiolation

Table 3: Comparison of Catalytic Efficiencies in Green Sulphur Transformations

Catalyst System	Reaction	Yield (%)	Temperature (°C)	Recyclability (Cycles)	E-Factor Reduction (%)
Pd/C (heterogeneous)	Aryl thiolation	95	50	10	80
$CuO\text{-}TiO_2$ (photoactive)	Thiol oxidation	88	30	8	70
$FeCl_3$ (homogeneous)	Aromatic sulfonation	92	60	—	65
NHC (organocatalytic)	Thiocarbonylation	90	25	6	75
Enzyme (biocatalytic)	C-S bond formation	85	37	12	90

3.2 Integration of AI and Computational Tools
Sulphur transformations with the help of computational chemistry and artificial intelligence (AI) are optimized by predicting solvents, energetics, and catalyst activities. Mechanisms of DFT calculations are explained at an atomic level. Machine learning (ML) models estimate the best reaction parameters, which decrease the amount of waste in the experiment. Sustainability metrics have been brought into synthetic planning in digital retrosynthetic tools like IBM RXN.

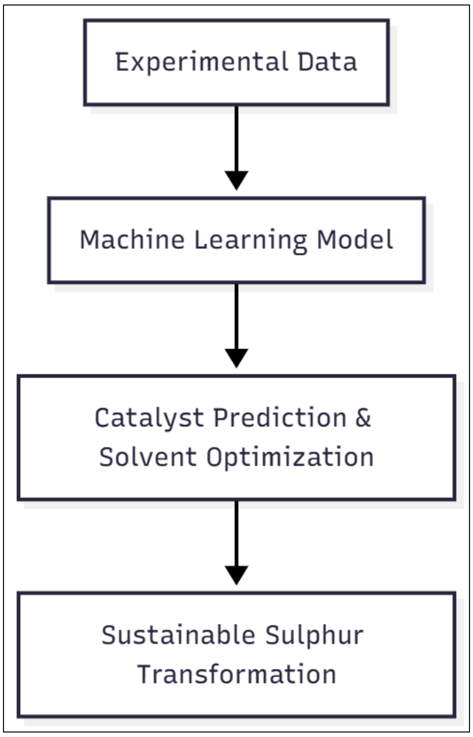

Fig 4: Integration of AI in Catalyst Optimization

Table 4: Green Metrics of Catalytic Sulphur Processes

Catalyst	Reaction Type	TON	TOF (h^{-1})	E-Factor Improvement (%)
Pd/C	Thiolation	2000	60	80
$g\text{-}C_3N_4$	Photocatalytic oxidation	1500	75	70
Ni Electrode	Electrochemical sulfonation	1200	55	76
Enzyme	Biocatalytic thiolation	2500	80	90

3.3 Quantitative Green Metrics
Atom economy (AE), E-factor, and process mass intensity (PMI) are used in order to measure the environmental performance of green sulphur chemistry. As an illustration, the solvent-free thiol-ene click reactions have E-factors lower than 5 in contrast to 40 in the traditional sulfonations (Capello *et al*., 2007) [3]. Greenhouse gas emission can also be decreased by 70 percent by adopting renewable input of energy as well as recyclable catalysts (Sheldon, 2018) [44].

4. Applications in Organic and Industrial Synthesis
4.1 Pharmaceuticals
Sulphur is the essential component of pharmaceuticals that has an impact on biologic activity and pharmacokinetics.

- Photo-reactive Sulfoxides and Sulfones: Peracids and toxic oxidants could be removed by photocatalytic oxidation with TiO 2 or by g-C3N4 (Xie *et al*., 2021) [47].
- Thioethers and Thiazoles: Pd/C and CuO - TiO 2 systems facilitate solventless synthesis, which minimizes waste (Li *et al*., 2020) [40].
- Sulfonamides: This generated flow synthesis on recyclable catalysts reduces the reaction time and the use of solvents (Jiménez-González *et al*., 2011) [5].

These developments are more economical of the atoms, selective, and more sustainable.

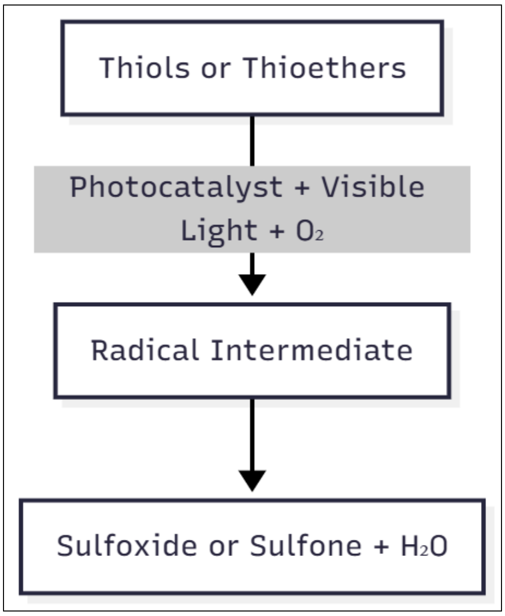

Fig 5: Pathway of Photocatalytic Sulfoxide Synthesis

Table 5: Examples of Sulphur-Based Drugs and Green Synthesis Approaches

Drug / Class	Functional Group	Traditional Issue	Green Synthesis	Reference
Omeprazole	Sulfoxide	Uses peracids, acidic waste	Photocatalytic oxidation (TiO_2, visible light)	Xie *et al*. (2021) [47]
Dapsone	Sulfone	Toxic oxidants	Electrochemical oxidation	Tay *et al*. (2022) [48]
Thiazoles	Thioamide heterocycle	Halogenated solvent waste	Solvent-free condensation	Yadav & Saha (2021) [50]
Methimazole	Thioimidazole	Acidic media	Enzymatic thiolation	Wong *et al*. (2022) [46]

4.2 Polymers and Functional Materials

The inverse vulcanization complete reaction and transformation of the elemental sulphur into poly (sulfurlimonene) and its derivatives that find use in optics and energy (Griebel *et al*., 2013) [13]. Using renewable alkenes, thiol-ene polymerization provides self-healing recyclable polymers with almost perfect atom economy (Hoyle and Bowman, 2010) [6]. These inventions reflect the re-processing of waste sulphur in to useful high-value products.

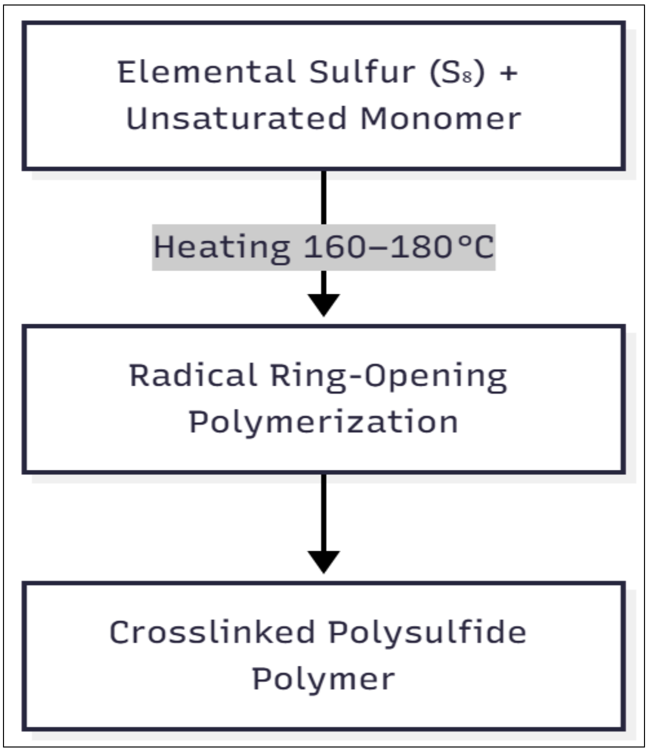

Fig 6: Process Flow of Inverse Vulcanization

Table 6: Sustainable Sulphur-Based Polymers and Applications

Polymer Type	Synthesis Method	Feedstock	Application	Green Feature
Poly(sulfur-limonene)	Inverse vulcanization	Elemental sulfur + limonene	Optical materials	Waste valorization
Thiol-ene networks	Photochemical polymerization	Thiols + alkenes	Coatings, adhesives	100% atom economy
Sulfur copolymers	Melt condensation	Sulfur + monomers	Energy storage	Solvent-free

4.3 Agrochemicals

The agrochemicals that contain Sulphur, including sulfonylureas and thiocarbamates are imperative to world agriculture. Microwave-assisted synthesis and or enzyme-mediated coupling lower the reaction time, wastes and toxicity (Yadav & Saha, 2021) [50]. Ionic liquids are useful as alternative to volatile solvents during organosulfate synthesis which can be recycled (Clarke *et al*., 2018) [2].

Table 7: Sustainable Sulphur-Based Agrochemical Routes

Agrochemical Class	Traditional Method	Sustainable Alternative	Benefit
Sulfonylureas	Acid condensation	Microwave-assisted synthesis	Reduced time & waste
Thiocarbamates	Solvent coupling	Enzyme-mediated	Aqueous conditions
Organosulfates	Chlorination routes	Ionic liquid catalysis	Recyclable solvent
Sulfones	Peracid oxidation	Electrochemical oxidation	Reagent-free

4.4 Energy and Environmental Technologies

The importance of sulphur materials in clean energy and mitigation of pollution increases. Li-S batteries use sulphur cathodes produced through a solvent-free melt diffusion, which has better performance and recycleability (Zhang and Zhao, 2018) [42]. Semiconductors doped with Sulphur serve as visible-light photocatalysts to produce hydrogen and eliminate pollutants. Moreover, mercury can also be captured using sulphur-limonene polymers on wastewater (Lim *et al*., 2019) [49].

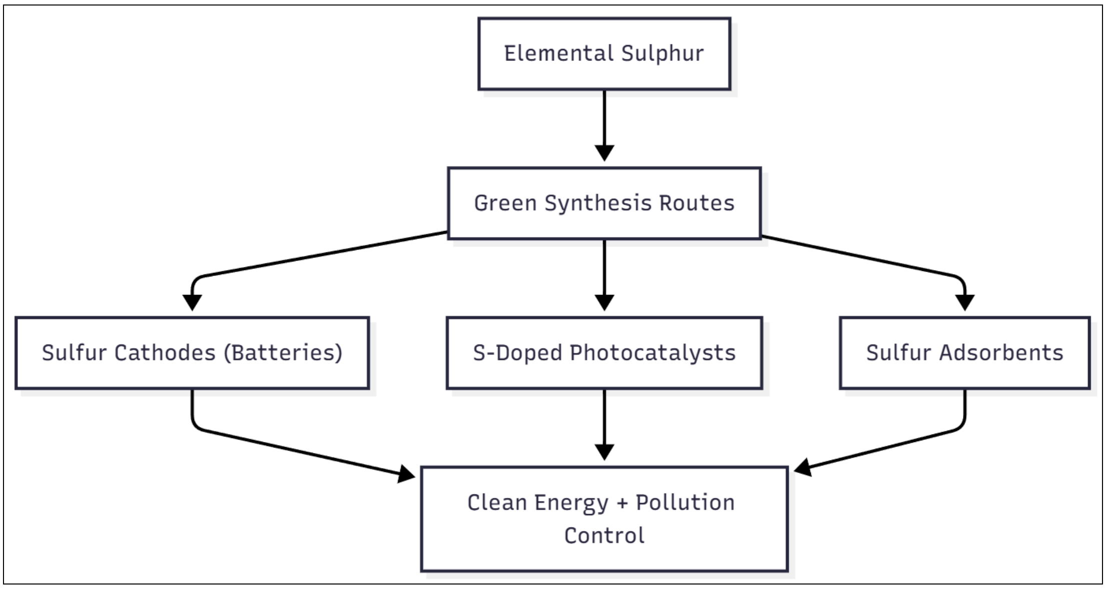

Fig 7: Sulphur in Energy and Environmental Systems

5. Environmental and Life-Cycle Assessment

5.1 Assessment Framework

Life-cycle assessment (LCA) measures sustainability within phases of the feedstock sourcing, production, use and disposal. The indicators of AE, E-factor, PMI, and carbon efficiency allow making comparisons between traditional and green processes based on data (Jiménez-González *et al.*, 2011) [5].

5.2 Comparative Environmental Impact

Research shows that there are great changes: E-factors go down to 12 at sulfonation and energy inputs decline by more than 60 percent when thermal heating is substituted with renewable systems (Capello *et al.*, 2007) [3]. Thiolation through bio-catalyzing and electrochemical sulfonation can reduce waste by 78% and result in 70% cuts in CO_2 emissions (Tay *et al.*, 2022) [48].

Table 8: Environmental Indicators Comparison Between Traditional and Green Processes

Process	E-Factor (Traditional)	E-Factor (Green)	PMI Reduction (%)	Energy Reduction (%)
Sulfonation	45	12	73	60
Thiol-ene click	20	5	75	55
Sulfoxidation	30	9	70	62
Electrocatalytic sulfonation	25	6	76	68
Biocatalytic thiolation	18	4	78	70

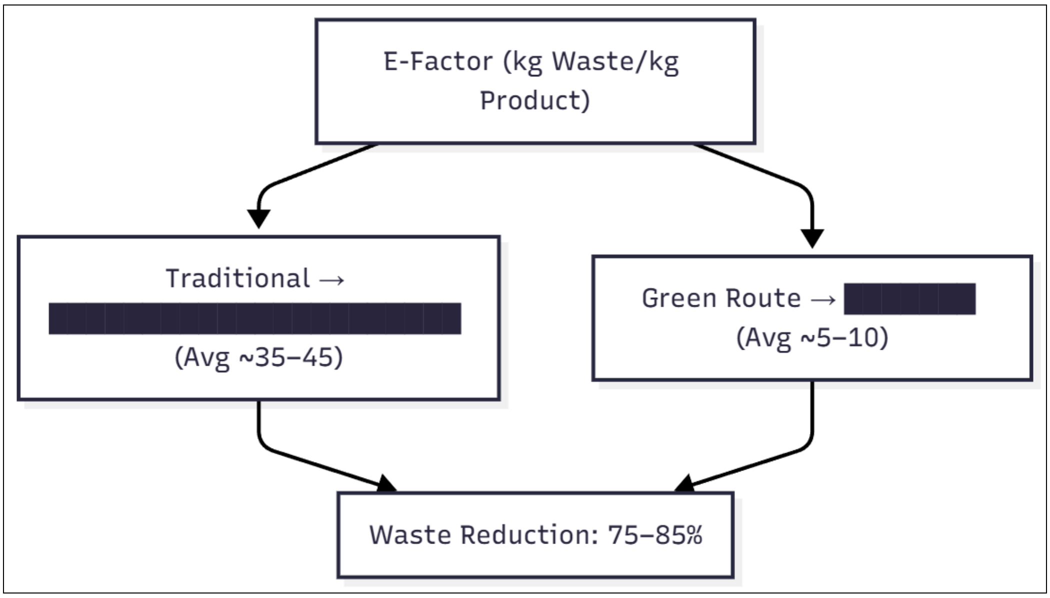

Fig 8: E-Factor Comparison Graph

5.3 Catalyst and Solvent Recovery

Recyclable ILs and DES minimize the losses in solvents by more than 90 percent, and the heterogeneous catalysts retain high turnover numbers over numerous cycles (Zhao *et al.*, 2021) [30]. With continuous bioprocessing, enzyme immobilization will ensure that only a minimal degradation occurs (Li *et al.*, 2020) [40].

5.4 Toxicity and Effluent Reduction
The environmental toxicity is reduced by using ethanol-water systems and solid acid resin, instead of chlorinated solvents and corrosive acids (Clarke *et al.*, 2018) [2]. Oxidation pathways are safer because the oxidant obtained is oxygen instead of peracids.

Table 9: Toxicity Reduction via Green Reagent Substitution

Chemical Agent	Traditional Use	Toxicity Level	Green Alternative	Reduction (%)
Chlorosulfonic acid	Sulfonation reagent	High (corrosive)	Solid acid resin	90
Dichloromethane	Solvent	High (carcinogenic)	Ethanol/DES	95
H_2O_2	Oxidant	Moderate	Photocatalysis (O_2)	100
Peracids	Oxidant	High	Biocatalytic monooxygenase	85

5.5 Circular Integration
The model of the circular economy can be recycling waste sulphur into polymers, fertilizers, and electrodes. The process of such upcycling translates the industrial waste to a useful resource, which improves the environmental and economic sustainability.

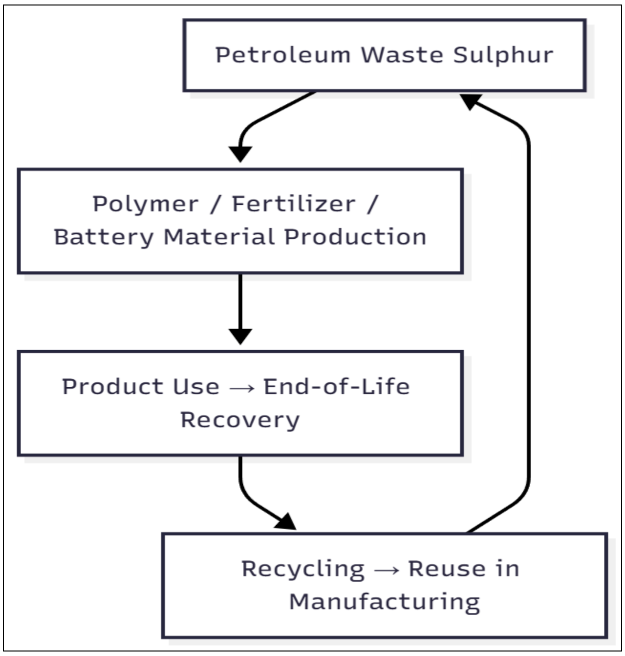

Fig 9: Circular Sulphur Economy Flow

6. Future Directions
6.1 Artificial Intelligence in Reaction Optimization
The design of catalysts, choice of solvents, and enzyme design now get informed by AI and ML. Predictive algorithms find the best parameters and approximate trials and experimentation by 70 percent, which are better. The systems allow optimization of E-factors, yields and energy efficiency to be automated.

Table 10: AI Applications in Green Sulphur Chemistry

Application	Objective	Example	Sustainability Outcome
Catalyst Screening	Identify optimal catalyst/ligand	ML-assisted Pd/C optimization	70% less waste
Solvent Selection	Minimize toxicity and GWP	Random forest model	Safer alternatives
Enzyme Engineering	Predict stability/activity	ML-guided biocatalyst design	Longer catalyst lifespan
Retrosynthetic Planning	Optimize reaction route	IBM RXN	Higher atom economy

6.2 Digital Twins and Smart Reactors
Digital twins are virtual copies of real-life reactors that observe the parameters of the processes and make changes dynamically Hagemann *et al*. Chemistry 4.0 is built with this technology, which makes it possible to conduct autonomous and adaptive green manufacturing (Sheldon, 2021) [51].

6.3 Flow Chemistry and Process Intensification
The continuous-flow reactor offers significant sustainability benefits: cut the reaction time by 85 percent, reduced solvents use by 75 percent, or energy use by 67 percent Stankiewicz and Moulijn,. Flow system enhances safety in dealing with reactive sulphur intermediates.

Table 11: Environmental Benefits of Flow-Based Sulphur Chemistry

Parameter	Batch Process	Flow Process	Improvement (%)
Reaction Time (min)	180	25	86
Solvent Use (L/kg)	12	3	75
Energy Input (kWh/kg)	420	140	67
E-Factor	25	7	72

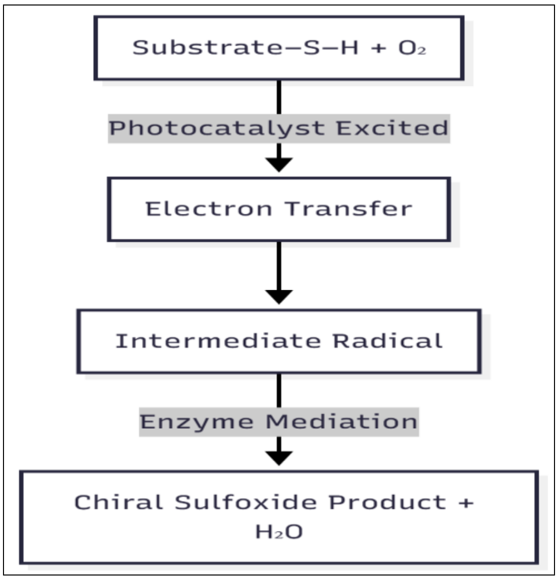

Fig 10: Biohybrid Catalytic Cycle

6.4 Biohybrid Catalysis

Biological selectivity will be paired with renewable activation with hybrid systems using enzymes with photocatalysts. These designs attain almost perfect selectivity in the visual light (Wong *et al*., 2022) [46]. The next synthesis frontier is biohybrid catalysis which involves biocompatibility and efficiency.

6.5 Renewable Energy Integration

The key aspect of carbon neutrality is electrocatalytic and photocatalytic systems that can be fuelled by renewable energy sources. Oxidants based on fossil are removed by solar driven oxidation and wind powered electrochemical sulfonation (Tay *et al*., 2022) [48].

6.6 Toward a Circular Sulphur Economy

Utilization of sulphur in closed loop transforms the byproducts produced in industries into new materials. A part of the sulphur that is recovered during desulfurization is reused to produce polymers and electrodes and produces zero-waste production (Lim *et al*., 2019) [49]. This solution will promote goal 12 of UN Sustainable Development Goal responsible consumption and production (UN, 2015).

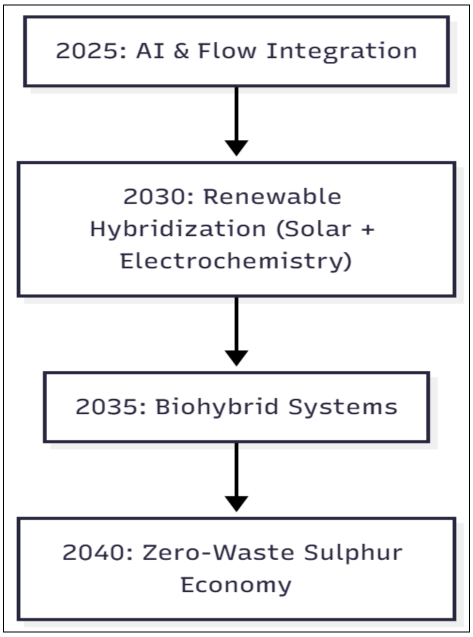

Fig 11: Future Roadmap: Circular Sulphur Economy

7. Conclusion

7.1 Key Findings

The high performance and sustainability can go together as evidenced by green sulphur chemistry. Several of the new rules include catalytic innovation, the redesign of solvents, and the acceptance of renewable energy, which reduced E-factors to up to 80% with atom economy reaching 100% (Sheldon, 2018) [44]. Life cycle statistics attest of over 60 per cent energy savings and more than 70 per cent carbon reduction (Capello *et al*., 2007) [3].

7.2 Integration of Green Principles

With the adoption of a set of principles, which include atom economy, catalysis, renewable feedstocks, and safer solvents, sulphur chemistry has been transformed into an exemplar of a sustainable synthesis (Anastas and Warner, 2000) [43]. The following are the examples of Biocatalytic, photocatalytic and electrochemical pathways where these principles are used.

7.3 Policy and Global Relevance
Green sulphur chemistry adheres to the major world frameworks like the UN Sustainable Development Goals, SDG 7 (Clean energy), SDG 9 (Industry and innovation), and SDG 12 (Sustainable consumption and production) (UN, 2015). It promotes carbon neutrality and waste material recycling.

7.4 Remaining Challenges
Although a successful story is documented, there are still setbacks: global efforts covered by the scale up, green solvents are expensive, and there are incomplete data in life-cycle assessment. This would require joint study of chemists, engineers and policymakers to be universal Clark *et al*.,

7.5 Future Vision
With the combination of AI-based automation, renewable energy and closed-loop, sulphur chemistry will be circular by 2040. This change will not only turn Sulphur into a non-polluting good but an ecological, and computer-friendly industrial resource, a symbol of a digital and sustainable chemical future.

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