

Metal oxide nano-cluster (polyoxometalates) as a versatile material for treatment of wastewater from textile dyes: A review

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(Dedicated to Late Prof. M. T. Pope for his pioneer work on polyoxometalates)

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Abstract:

Textile dye-containing wastewater is a major challenge today due to its high toxicity and chemical stability. Polyoxometalates (POMs) are anionic polynuclear metal-oxygen complexes made of early transition metals in high oxidation states, typically built from corner and edge-sharing MO₆ octahedral units. These metal oxide polyanions are widely recognized for traits such as strong redox behaviour, structural tunability and catalytic activity under light and electrochemical conditions. This review provides a detailed overview of current studies on the application of POMs and POM-based materials, such as MOF-composites, for the degradation of textile dyes from wastewater. Dyes are classified based on their charge, i.e., cationic dyes - positively charged, anionic dyes - negatively charged and non-ionic dyes - neutral dyes, with literature-reported studies focusing on Methylene Blue, Malachite Green, Rhodamine B, and Crystal Violet as cationic dyes, and Congo Red and Methyl Orange as anionic dyes. Azo dyes are discussed separately in detail due to their large-scale usage in the present-day textile industries. The mechanisms involved in dye removal - adsorption, photocatalytic, electrochemical process, and Fenton-like reaction are discussed. Studies on electro-Fenton and photoelectron-Fenton processes, incorporating POMs have shown extremely high efficiencies in the degradation of industrial dyes because of their enhanced reactive oxygen species generation and enhanced catalytic stability. Factors affecting dye degradation, initial dye concentration and adsorbent concentrations, the effect of pH change and temperature dependence are also explained briefly. Additionally, adsorption isotherms, adsorption kinetics, and desorption studies are discussed to test dye-POM interactions and material reusability. The review highlights the potential of POM-based systems for efficient dye degradation and outlines the direction for future research.

Keywords: *polyoxometalates, tungstate, wastewater treatment, dye degradation, Methylene blue, Congo red*

1. Introduction

Industrial wastewater is a major concern for the environment because of the increasing use of synthetic dyes in a lot of industries like textile, leather, paper, tannery, paint, dyeing and other industries [1]. The increasing demand of the world's growing population has led to rapid growth in industrial advancements and caused accidental or incidental small- or large-scale discharge of dyes into the natural environment [2]. Dyes constitute a major component in the wastes released by multiple textile manufacturing plants, which pose high risks to the open water bodies [3]. Many industries, especially textile, paper, dyeing, paints and leather, use water that contains a mix of harmful substances [4]. Among all the pollutants, dyes are particularly difficult to remove as they are highly visible, even in small amounts, and they color all the water content [5]. Many dyes are non-biodegradable, toxic, unaffected by sunlight, mild acids, mild bases, and microbial breakdown [6]. These different coloured dyes can block sunlight from entering water and disrupt photosynthesis in aquatic plants, resulting in ecosystem imbalance [7]. Most industries use synthetic dyes- chemical compounds designed to be vibrant and long-lasting, but these dyes are washed out during the manufacturing process and end up as wastewater [8-9]. Textile dyeing and finishing industries from industrial sources are invariably reported as the maximum contributors to dye-containing wastewater, followed by dyeing units, pulp and paper, leather, and allied sectors [10-12].

Dyes used in Industrial processes can be broadly classified as organic and inorganic dyes, each with its own environment and health risks [13]. Organic Dyes such as Azo Dyes, Anthraquinone Dyes, and Triphenyl Methane Dyes are commonly used colorants in textile, paper and leather industries as they make bright color, high resistance to biodegradation and low cost. These dyes often undergo photochemical and microbial transformations to form intermediates that are toxic, carcinogenic and which threaten aquatic life and human health through bioaccumulation and contaminated water supplies [14]. On the other hand, inorganic dyes are less commonly used because they contain metallic pollutants like Lead (Pb²⁺), Mercury (Hg²⁺), Cadmium (Cd²⁺), and Chromium (Cr³⁺), which are toxic even at low concentrations [13]. When released into water bodies, these dyes degrade water quality by imparting color, making the water unsafe for drinking, contributing to metal toxicity, disrupting aquatic food chains, and posing long-term environmental risks [15]. Over the years, various methods-including adsorption, membrane filtration, advanced oxidation processes (AOPs), electrochemical treatment, and microbial or enzymatic degradation have been employed for wastewater treatment. Even with all the efforts, traditional methods face limitations like high cost, incomplete removal of dye, great demand for catalysts, waste generation, and cloudy water [14], [16-19].

To address the persistent challenges posed by industrial dye wastewater, several research projects are going on to find advanced and sustainable treatment techniques. Nanomaterials like metal organic framework (MOFs), Carbon Nanotubes (CNTs), and Graphene Oxides (GO) are observed to have great effects in increasing adsorption and catalytic degradation of complex dye molecules [20-22]. Using sunlight with materials like TiO_2 and ZnO is another effective method that helps turn dyes into harmless byproducts [23]. Additionally, researchers are testing bacteria and enzymes that can selectively target dye pollutants, offering a more precise and environmentally sustainable approach to wastewater treatment technologies [24]. Still, making these methods work on a large scale, keeping costs low, and ensuring they last a long time are big challenges. So, there is a great need to step up the work and find sustainable and novel materials to bring a revolution in the traditional methods of wastewater treatment.

POMs are strictly polynuclear metal-oxygen complexes. Generally, these are early transition metals of the periodic table in their highest oxidation states [25]. They can have any heteroatoms, e.g., silicon (Si), Phosphorus (P), and Arsenic (As). POMs have unique physical and chemical properties like strong Bronsted acidity, redox activity, molecular polarity and surface charge distribution, stable and reversible electron/proton storage, high thermal stability [25-27], Structural properties like well-defined atomic structure, dynamic structure, diverse and controllable composition [28-30]; and Functional Properties like catalytic activity, photocatalysis, biomedical applications and electronic and optical properties [29], [31-33]. These unique properties bring significant attention towards polyoxometalates in various fields of study like chemistry, biology, catalysis, material science, molecular electronics, environmental remediation and energy storage [34-35]. Among the studies, Keggin structure appears predominant. The Keggin type POMs have general formula $[\text{XM}_{12}\text{O}_{40}]^{n-}$, where X is the central heteroatom (e.g., P, Si, Ge, As) and M is the addenda metal, typically Mo or W. The structure consists of a central XO_4 tetrahedron surrounded by twelve MO_6 octahedra, which are organised into four M_3O_{13} triads. Each triad is composed of three edge sharing octahedra, and four triads are interconnected through corner sharing oxygen atoms, resulting in the characteristic tetrahedral symmetry of the Keggin anion. In addition to Keggin framework, several other POM structures, e.g., Wells-Dawson, Anderson-Evans and Lindqvist, have been reported [36]. Their respective structures are illustrated in Figure 1. Structural study can provide a more selectivity for the type of dye needed to be degraded.

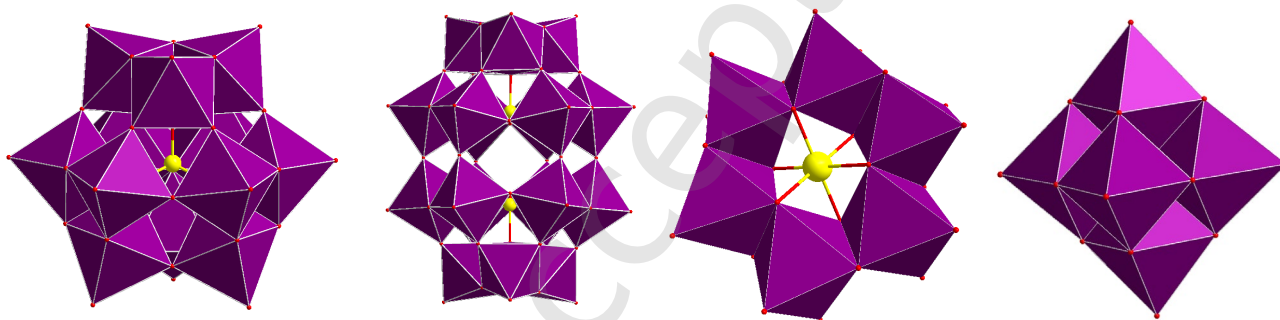


Figure 1: Different POMs Structures including Keggin, Wells-Dawson, Anderson-Evans and Lindqvist. Adapted from [36] under the Creative Commons Attribution 3.0 (CC BY 3.0) License.

In the last few years, polyoxometalates have been addressed as promising candidates for dye degradation because of their unique properties, such as redox property, structural property, and ability to participate in multiple catalytic reaction mechanisms. Recent research highlights that POMs enable more efficient industrial wastewater treatment when added to composite materials [37]. In some studies, POMs photocatalytic activity is reduced due to low surface area and stability, so substrates like MOFs [38-39], graphene [22], [40-41], silica [42-43], etc., are used to increase their surface area and overall photocatalytic activity. Year wise evolution of POMs based water treatment strategies is shown in Figure 2.

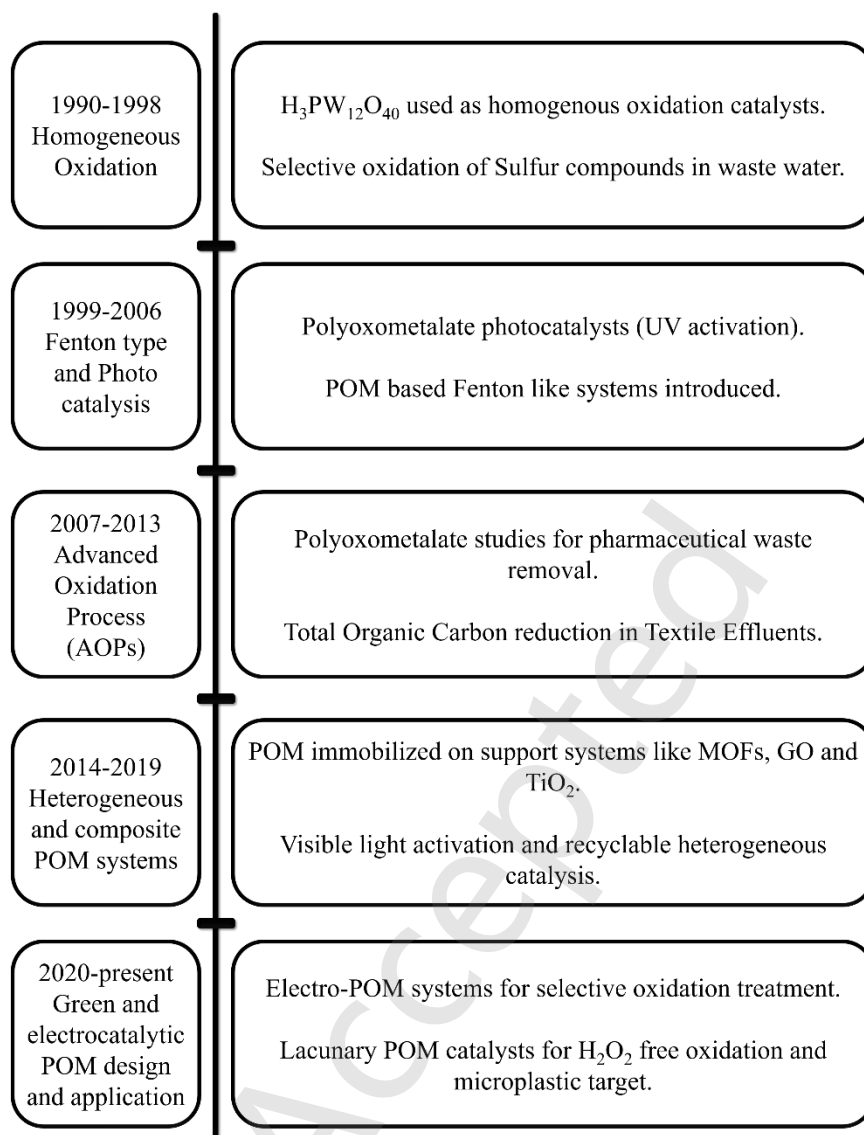


Figure 2: Evolution of POM-based waste treatment strategies during the years.

In this review, we have systematically summarized all the recent progress in designing and sustainable environment applications of polyoxometalate photocatalysts and their composites with metal organic framework. Special attention is given to their structural diversity and their degradation efficiency in various classes of dyes, i.e., Cationic Dyes, Anionic Dyes, Non-Ionic Dyes, and Azo Dyes.

2. Industrial Dye Classification by Charge

Industrial dyes are complex organic compounds that are heavily used in textile industries, leather industries, paper industry, plastic industry, printing industry, and dyeing industries to impart colour and brightness to the substrate [44]. However, properties like high stability, synthetic origin, and resistance to biodegradation make them major pollutants in industrial wastewater [3].

Dyes can be classified based on their source, like natural and synthetic, chemical structures and method of application as shown in Figure 3 [45]. Dyes can be classified further by structural diversity as azo dyes, anthraquinone dyes, indigoid dyes, phthalocyanine dyes, sulfur dyes, nitro and nitroso dyes [46-49]. They have two groups in chemical structure, chromophores and auxochromes. Chromophore is responsible for giving colour to the substrate, and auxochromes are responsible for changing the intensity of the color from the chromophore [50]. Further dyes can be classified based on their application method as reactive dyes, dispersed dyes, acid dyes, basic dyes, direct dyes and vat dyes [46-49]. Dyes can also be classified by their ionic character as cationic, anionic, or non-ionic dyes [56]. Azo dyes are discussed separately because of their extreme use in industries. They include both cationic and anionic dye classes and account for approximately 70% of the dyes manufactured worldwide [51-52]. Understanding their classification and chemical characteristics is important for designing effective photocatalytic and adsorption degradation systems, such as polyoxometalate-based materials. The studies mentioned in Table S1 in the Electronic Supplementary (ESM) are not reviewed in comparison, but singled out to emphasize the structural variability of polyoxometalates and experimental conditions (like pH, catalyst and dye dosage, Temperature, Process and Efficiency) as they have been applied in wastewater treatment from dyes.

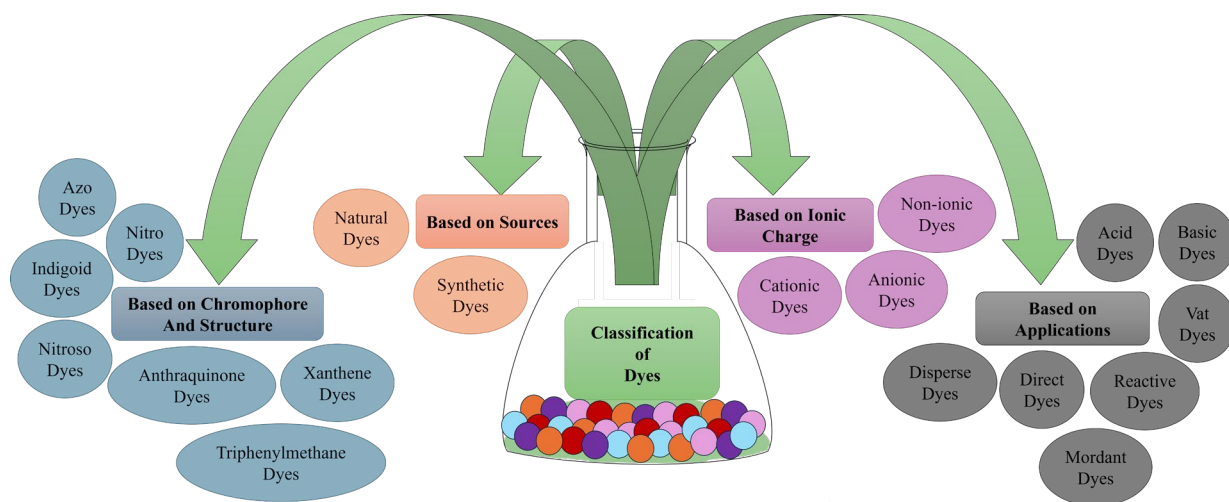


Figure 3. Dyes classified by sources, structure and chromophore, ionic charge and application method.

2.1. Cationic dyes:

Dyes can either be charged (positive or negative), or neutral. It can be cationic, anionic or non-ionic depending on the charge it carries [53]. Cationic dyes are positively charged. They are basic in nature and are generally seen in the ZnCl_2 or HCl complexes[54]. Methylene Blue [55], Malachite Green [56], Rhodamine-B [57], Rhodamine-6G [58] are heavily researched under cationic dyes. All these dyes are toxic in nature and capable of imparting color to water even in small amounts.

2.1.1. Methylene blue:

Prolonged exposure to methylene blue dye is reported to be associated with some psychological effects, highlighting the need for sound elimination of dyes in the environment. The studies from 2017 to 2026 collectively highlights the versatility of POM based materials for MB dye degradation, yet no comparison is possible in between studies because of inconsistent experimental parameters and different dye removal mechanisms. Contact time variation is too enormous to compare, 1 minute (Guo *et al.* [59]) to 48 hours (Zhai *et al.* [60]), suggesting different physiochemical processes rather than simple adsorption or photocatalytic activity. Saad *et al.* [61] operated at pH 1, raising environmental relevance concerns. Notable, Murmu *et al.*[62] reported only 32-36% degradation efficiency for $\text{Na}_2\text{W}_6\text{O}_{19}$ which is contrasting sharply with other tungstate systems. As summarized in Table S1 in the ESM, despite impressive individual efficiencies, the absence of ambient condition significantly limits the practical applications.

2.1.2. Malachite green:

Malachite green dye is the most widely used dye in the clothing industry, the fish industry and for extreme use as a disinfectant in the medical sector. Malachite green dye is also known to have carcinogenic properties and the ability to cause mutation [56],[63-64]. POMs have been effectively used in the photodegradation of MG. Polyoxometalate hybrid materials are efficient photocatalysts for Malachite Green dye degradation due to their unique properties, such as tuneable redox properties, electron sponge property, and structural versatility. Hybrid-POMs with layered double hydroxides(LDHs), semiconducting oxides and transition metal centres significantly increase the catalysts performance in adsorption, increase charge separation and promote ROS formation. POM-LDH composites show strong synergistic adsorption-photocatalysis behaviour. ZnAl-LDH supported Keggin type POMs such as $\text{SiW}_{12}\text{O}_{40}$ and $\text{PW}_{12}\text{O}_{40}$ show good MG dye removal efficiencies in near neutral conditions due to the electrostatic interactions between positively charged LDH layers and polyanions. LDH also improve catalysts stability by reducing POM aggregation and leaching [65].

Various metal oxide-based nanomaterials, including those combined with polyoxometalates, have been applied for the photocatalytic degradation of Malachite Green Dye. These studies often involve optimizing conditions such as pH, catalyst dose, and light source to achieve high degradation efficiency. For example, $\text{La@Fe}_2\text{O}_3/\text{TiO}_2$ composites showed a 78.62% photodegradation efficiency under UV-Visible light [66]. In 2016, Liu *et al.* [67] synthesized $(\text{NH}_4)_5[\{\text{PW}_{11}\text{O}_{39}\} \text{Mn}^{\text{II}}(\text{H}_2\text{O})]$ (Mn-POM) and $(\text{NH}_4)_5[\{\text{PW}_{11}\text{O}_{39}\} \text{Zn}^{\text{II}}(\text{H}_2\text{O})]$ (Zn-POM). Both are used as photocatalysts to activate O_2 for the degradation of dye molecules under visible-light. $(\text{NH}_4)_5[\{\text{PW}_{11}\text{O}_{39}\} \text{Mn}^{\text{II}}(\text{H}_2\text{O})]$ (Mn-POM) achieved 74% of degradation of malachite green dye in 30 minutes while $(\text{NH}_4)_5[\{\text{PW}_{11}\text{O}_{39}\} \text{Zn}^{\text{II}}(\text{H}_2\text{O})]$ (Zn-POM) achieved 90% degradation of malachite green dye in same amount of time.

2.1.3. Crystal violet:

Use of Crystal Violet is scalable in dyeing in textile industries, antiseptic, and as a stain in biological or biotech studies. It is highly toxic and non-biodegradable. It is known to exhibit mutagenic, carcinogenic, and cytotoxic properties and can cause severe irritation to the eyes and skin, along with harmful effects on the aquatic biota [68]. LDH supported POM composite, i.e., Tris-LDH- PW_{12} shows rapid degradation of Crystal Violet dye in 5 minutes. This is because of strong electrostatic attraction between dye molecule and positively charged LDH layers, which enhances interfacial interaction with catalytically active phosphotungstate units. LDH structures improve POM dispersion, suppress agglomeration, enhance stability and facilitate electron migration which leads to less electron hole recombination [69]. Mesoporous supports like MCM-22 significantly boost POM photocatalytic performance by increasing the surface area, improving pore accessibility and distributing active sites more effectively. Since Crystal Violet is a

cationic dye, electrostatic interactions play a key role in driving its adsorption and degradation. Immobilizing SiW₁₂ units within MCM-22 stabilize the catalyst structure and minimize the leaching during aqueous treatment. POMs naturally promote charge separation and oxidative activation under UV and Visible light due to their electron sponge character [70].

2.1.4. Rhodamine B:

This is a synthetic xanthene dye widely used as an industrial dye in textiles, paper and cosmetics. It is known to be toxic and has been reported to cause skin and eye irritation, hepatotoxicity and potential carcinogenic effects upon long-term exposure. It is also environmentally persistent and poses serious risks to aquatic biota [71-72]. Keggin type PW₁₂/TiO₂ [73] composites degrade Rhodamine B efficiently by using POM units as electron acceptors that reduce the recombination and increase the charge carrier lifetimes. Porous structure improve surface accessibility and adsorption. H₂O₂ activated PW₁₂/SiO₂ systems support ROS generation through per oxo intermediates while silica support improve dispersion and stability. Zn/POM heterostructures with Ag₄SiW₁₂O₄₀ or Cs₃PW₁₂O₄₀ boost visible light response and charge transfer [74]. Degradation propagates as ROS mediated demethylation, chromophore cleavage and mineralization. Structural features like heteroatom, lacuna presence influence the efficiency.

2.2. Anionic dyes:

Anionic dyes are widely used for industrial processes, particularly in the textile industry, leading to significant environmental concerns due to the generation of toxic dye wastewater. These dyes have a negative charge on them that interacts with substrates and absorbates [75-77]. Anionic dyes pose significant risks to the environment because of their complex aromatic structures that make them hard to remove. They exhibit toxicity, mutagenicity, genotoxicity and impact human health and aquatic biota [77-78]. This discharge of wastewater leads to water pollution and affects water properties, aquatic species and human life [76,79].

2.2.1. Methyl Orange:

Methyl orange (MO), Sodium 4-[[4-(dimethylamino)phenyl] diazenyl] benzenesulfonate, is an acidic azo dye that is characterized by the presence of an acidic sulphonic group as auxochrome. TiO₂ supported heteropolyacid composites have emerged as some of the best options for photocatalytic dye degradation as seen in Table S1 in the ESM. The Keggin type PW₁₂ units show electron sponge behaviour by soaking up photogenerated electrons from TiO₂ before they can combine with holes. It keeps ROS production running efficiently. Porous structures provide better access for dye molecules towards the active centres. Swapping an addenda atom with cobalt or vanadium makes the catalyst even more capable as these metals are naturally good at absorbing electrons and activating oxygen. Adding H₂O₂ to PW₁₂/SiO₂ systems create excited per oxo species that can easily break the azo bonds. Since MO carry a negative charge, catalyst with positive surface naturally attracts and degrades it more efficiently. Polyanions or POMs are highly anionic species. To overcome negative charge generally POMs are incorporated in positively charge materials, sheets or support materials [80-83].

2.2.2. Congo Red:

Congo Red is a synthetic dye with diazo bonds (-N=N-) in its structure, contributing to its high toxicity and carcinogenicity properties. Congo red has been used in dyeing cotton, as a pH indicator and as a biological stain. It is known for its stability and resistance to biodegradation. Congo red is highly toxic and carcinogenic; it poses significant environmental risks when released untreated into the environment. It is resistant to biodegradation processes. PW₁₂/TiO₂ structures offer greater surface exposure, allowing Congo Red adsorption on the active sites, while g-C₃N₄ and Fe₃O₄ supported heteropoly anions opens up possibilities like efficient charge separation and easy recyclability of catalysts. Hydroxyl and superoxide radicals are primary responsible for azo bond cleavage. Since Congo Red is anionic, catalysts with positively charged sites exhibit enhanced adsorption affinity and degradation kinetics. Copper substituted POM frameworks additionally improve electro transfer and ROS production by modifying the electronic structure, collective strengthening overall photocatalytic performance [84-85].

2.3. Non-ionic dyes:

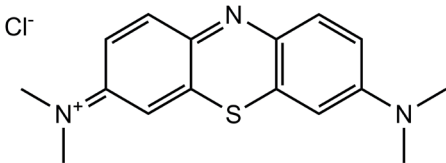
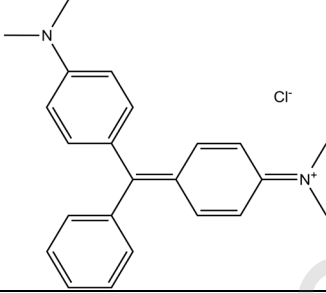
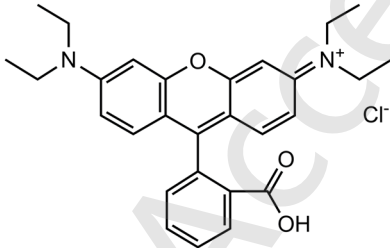
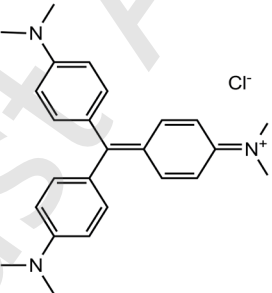
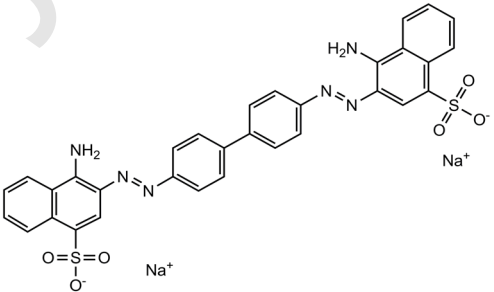
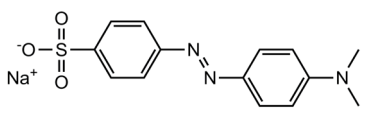
Non-ionic dyes represent a class of pollutants that are electrically neutral in aqueous solutions. These dyes do not possess ionizable functional groups like sulfonates (SO₃⁻) or ammonium group (NH₄⁺) [86]. Their chemical structure relies on hydrophobic interaction and hydrogen bonding [87-89]. The degradation of non-ionic dyes, especially vat dyes like indigo, requires more than simple surface adsorption; the catalyst must follow multi-step electronic rearrangements [90]. Polyoxometalates are suited for this due to their role as molecular electron sponges [91]. Despite the superior redox capabilities of polyoxometalates, their application in degrading Indigo, a cornerstone of the denim industry, is comparatively low in comparison to model dyes like methylene blue and rhodamine-B [43],[92-93]. Many studies focus on the use of polyoxometalate as an oxidant for the dye molecule. Indigo often requires an initial reduction step to make it a soluble leuco indigo derivative before it can be mineralized. Most POM research is not yet optimized for dual-stage redox pathways for textile dyes [94-96].

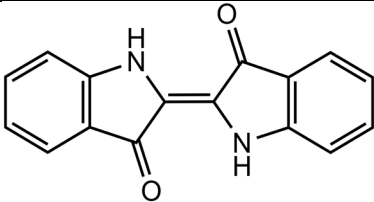
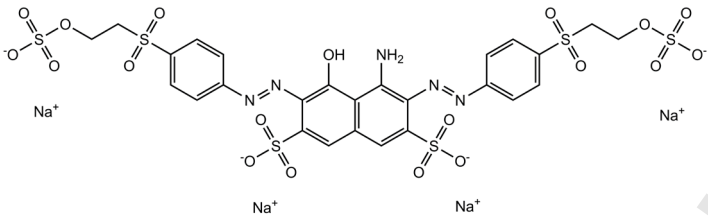
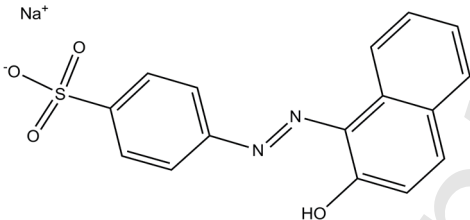
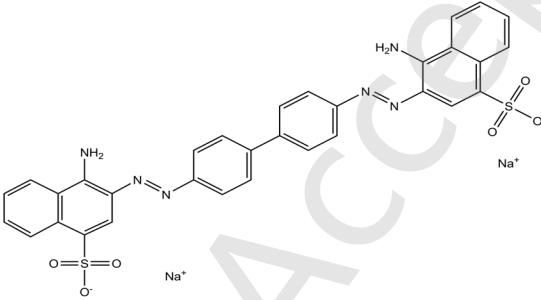
2.4. Azo dyes:

Azo dyes cover a large group of nearly all major dye classes, including acidic, basic, and ingrain(naphthol) dyes. These are identified by the presence of azo linkage (-N=N-) in the chemical structure. They cover over 70% of dye stuff [97-98]. Numerous azo dyes are used in many different industries. Methyl orange is the most common example of water-soluble azo dyes (used to test pH). It is widely used in industries related to paper manufacturing, the food processing industry, textile colorant and printing sectors [99]. Table 1 explains the major industrial use of different dye classes discussed above [99]. The textile sector uses Acid orange 7 to color silk, wool and nylon. Additionally, it is used as a colourant in leather and paper goods. Market analysis reports show a sustainable growth in the global demand for Acid Orange dyes, primarily due to the continuous use in textile and allied industries in the coming decade.

Azo dyes degrade mainly through oxidation of azo bonds by photocatalysis or Fenton pathways. Photocatalytic dye degradation using POMs depends primarily on architecture, transition metal incorporation, porosity and active site accessibility. Porous systems, like MCM-22 molecular sieves incorporating SiW₁₂ enhance performance through greater surface area, lower POM aggregation, efficient reactant diffusion. Cobalt (II) and Zinc (II) based supramolecular assemblies improve charge transfer and forms multiple simultaneous adsorption-oxidation sites, with cobalt system excelling due to superior redox flexibility, electron mobility and stability. Poloxovanadate and Polyoxomolybdate catalysts demonstrate strong oxidative performance, as vanadium and molybdenum centres efficiently activate oxidants and generate hydroxyl radicals that cleave azo bonds. Overall degradation proceeds through reactive oxygen species (ROS) mediated oxidation, followed by fragmentation and mineralization of intermediates, as demonstrated with dyes including Chrysoidine and Amido Black 10B [60],[70],[100-101].

Table 1 Dyes classified by ionic nature, along with their industrial uses

Dyes	Structure	Industrial Uses	Ref.
Cationic Dyes			
Methylene Blue (MB)		Dyeing of cotton, silk, and wool. Paper and leather coloration. Used as a biological stain and redox indicator.	[102-104]
Malachite Green (MG)		Dyeing of wool, silk and leather, Paper and fibres. As an antimicrobial agent in aquaculture (now banned).	[63]
Rhodamine B (RhB)		Dyeing of synthetic fibres (polyester, acrylic). Tracer dye in textile and water studies. Pigments and inks (limited textile use today due to toxicity).	[105-106]
Crystal Violet (CV)		Dyeing of cotton, silk, wool, and paper. Printing inks and paints. Biological staining applications.	[107-108]
Anionic Dyes			
Congo Red (CR)		Dyeing of cotton and paper. Textile Printing. Indicator dyes in laboratories.	[109]
Methyl Orange (MO)		Dyeing of textiles and paper. Used mainly as a pH indicator. Model azo dye in wastewater studies.	[110-111]
Non-Ionic Dyes			

Indigo		Dyeing of denim (cotton textiles). One of the most widely used textile dyes globally. Major pollutant from jeans manufacturing wastewater	[112]
Azo Dyes			
Reactive Black 5 (RB5)		Widely used in the reactive dyeing of cotton and cellulose-based textiles. Common in textile printing and finishing processes. Highly water-soluble, leading to intense colouration of textile effluents. Frequently used as a model azo dye in wastewater treatment studies.	[113-115]
Acid Orange 7 (AO7)		Used for dyeing wool, silk, nylon, and leather. Applied in acid dyeing processes in textile industries. Also used in printing inks and laboratory studies. Considered a recalcitrant azo dye due to its aromatic azo linkage.	[116-118]
Direct Red 28 (DR28)		Used for dyeing cotton, viscose, and paper. Applied without mordants, making it common in direct dyeing processes. Produces highly coloured wastewater due to poor fibre fixation. Often selected as a representative direct azo dye in degradation studies.	[119-121]

3. Mechanism for dye degradation:

Wastewater mixed with dye effluent can cause a potential hazard to the environment. Therefore, many physicochemical techniques were developed to clear the wastewater for addressing the issue. Physiochemical methods like ion exchange [122], and adsorption [123] and chemical methods like photocatalytic processes [124-125] are widely studied for the degradation of dyes from wastewater. Each of these methods has limitations like high cost, operational design, and dye degradation efficiency [122], [126-127].

Among the various treatment techniques, adsorption is the most effective and practical method for dye removal because of its many advantages compared to other methods. The advantages and disadvantages of different techniques are mentioned in Table 2. Table 3 explains the dominant dye's interaction with POMs and the dominant removal mechanisms.

Table 2 Separation mechanisms and their advantages and disadvantages [54, 128, 129]

Principle	Key Benefits	Limitations
Chemical methods		
Photo Catalyst	Cost-effective and does not produce sludge	Some photo catalysts break down into harmful by-products.
Fenton-like reaction	Inexpensive reagent and efficient process	Problems related to the disposal and formation of sludge
Physical-chemical methods		
Adsorption/Sorption	High adsorption capacity and effective for many dyes	Limited surface area in some Adsorbents, High Adsorbent cost. Need for adsorbent disposal.
Membrane filtration	Effective against all dyes	Suitable for treating low volume but involves sludge formation.

Table 3 Representation of different dyes' interaction with POMs and dominant removal mechanism

Dye Type	Interaction with POM	Dominant Removal Mechanism	References
Cationic (+)	Strong adsorption	Adsorption	[130-131]
Anionic (-)	Weak adsorption	Photocatalytic	[131-132]
Azo	Breaks at -N=N-	Photocatalysis, Fenton-like	[96]
Triarylmethane	Strong π - π interactions	Adsorption, Electrochemical	[132-134]
Xanthene	Visible-light absorption	Photocatalysis, electrochemical	[135]

3.1. Adsorption of dye:

Adsorption is one of the most common methods for waste processing in many industries. This technique allows the selective removal of dissolved components from liquids by accumulating them on the surface of the solid material. The adsorbent may be liquid, solid or gas or may be a solute dissolved in the aqueous solution. Generally, adsorption is characterized as physical adsorption and chemical adsorption [136]. Chemical adsorption occurs due to electron exchange between the adsorbate and the adsorbent, where the adsorbate gets chemisorbed on the surface of the adsorbent [137]. In physical adsorption, contaminants are adsorbed on the adsorbent surface by weak intermolecular forces like hydrogen bonding and dipole-based interactions. The extent of adsorption depends on molecular mass, dimensions, structural characteristics, solute concentration and polarity of the adsorption system [54], [128-129].

The primary mechanism for dye adsorption for the removal of dye is based on the adsorption phenomenon by polyoxometalates, which involves interaction between the anionic polyoxometalate catalyst and the cationic dye molecule. This POM-Dye interaction is important for the adsorption of cationic dyes [131]. A schematic representation of the adsorption mechanism and surface activation of polyoxometalate is shown in Figure 4. These dyes are attached to the surface of polyoxometalates, and this property offers advantages like high efficiency, recyclability and easy operations [132]. As suggested in the last step of Figure 3 where both H^+ and the dye cation (DYE^+) carry a positive charge. However, the size of cation plays an important role in the adsorption process. Owing to its significantly larger size than H^+ , DYE^+ exhibits greater tendency to adsorb onto the larger POM catalysts. The rate of adsorption decreases with time as the number of available sites on the adsorbent gets covered with adsorbate. With time, equilibrium gets established between the dye molecules remaining in solution and those adsorbed on the surface of the adsorbent. The overall adsorption performance is therefore affected by factors such as surface area, pore structure, and contact time [133] and initial dye concentration [134]. This separation technique is widely applied for the removal of dyes from aqueous solutions. The performance is determined by physicochemical characteristics of the adsorbent-adsorbate pair along with parameters like market cost, subject availability, convenience of operation, surface area and toxicity [135]. Due to its simple design, ease of operation and convenience, adsorption is frequently used in wastewater treatment [136–138]. This property is advantageous to reduce energy requirements, particularly in most developing countries that lack an appropriate amount of energy [139–141].

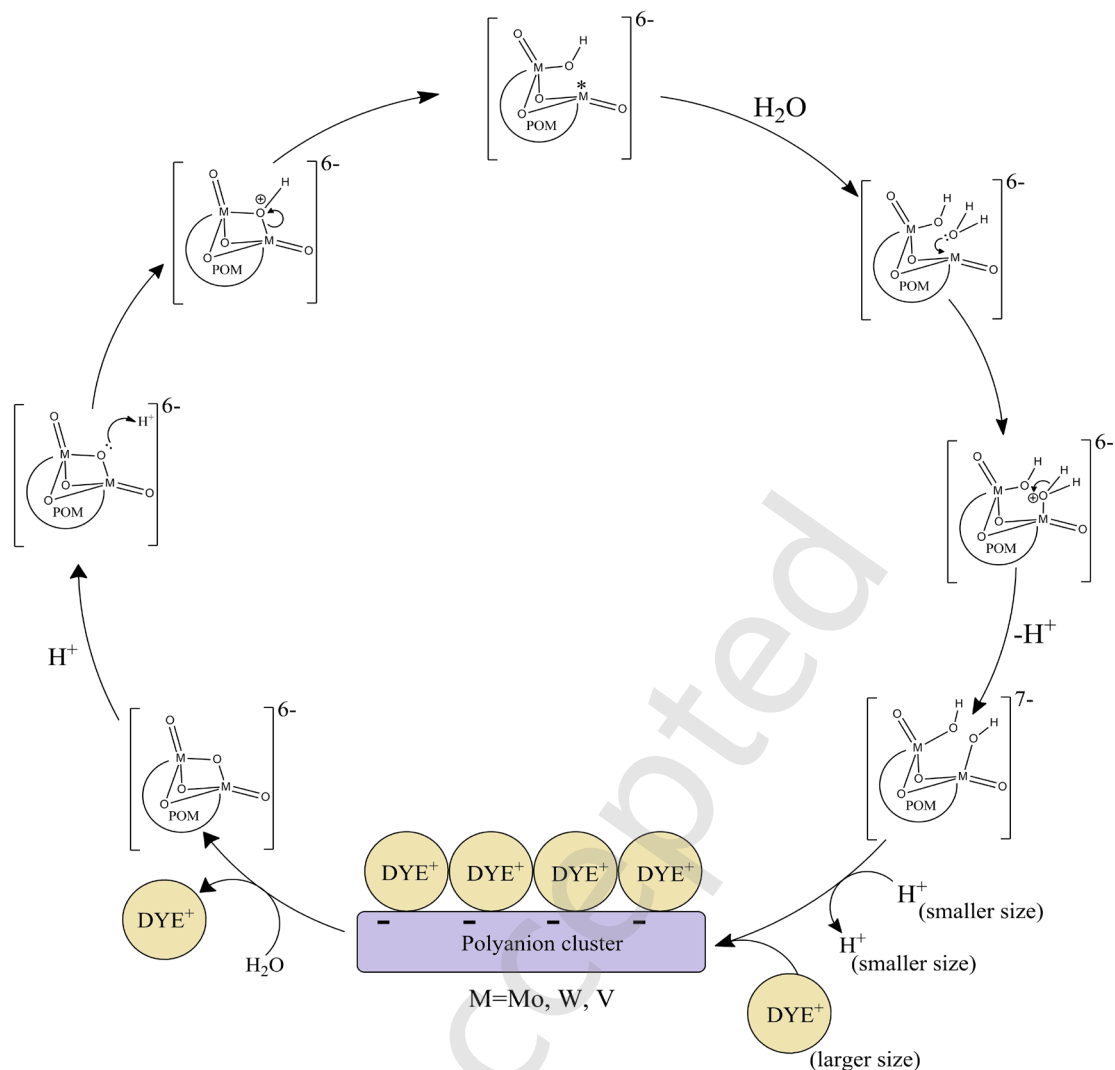
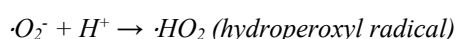
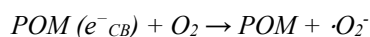


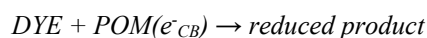
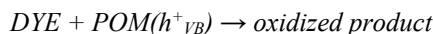
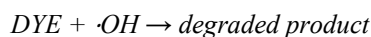
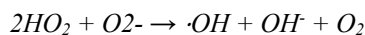
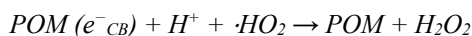
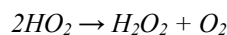
Figure 4: Schematic mechanism of Dye adsorption on Polyanion.

3.2. Photocatalytic Mechanism:

Photocatalytic degradation experiments are conducted under a UV or visible light source. To achieve maximum degradation, experiment parameters like dye concentration, catalyst concentration and pH are optimized [142]. Polyoxometalates promote the generation of reactive oxygen species (ROS), including hydroxyl radicals ($\text{OH}\cdot$) and superoxide anions ($\text{O}_2\cdot^-$), upon light activation. These generated radicals are primarily responsible for oxidation and the breakdown of dye molecules [143]. On light irradiation, POMs generate electron hole pairs, the hole in the valence band and electrons in the conduction band, especially in redox reactions, leading to the formation of ROS [144]. In some studies, dye molecules can act as photosensitizers, transferring photoexcited electrons to the photocatalyst conduction band, resulting in high degradation efficiency [145].

Photocatalysis refers to the light-induced activation of polyoxometalates, where photon absorption exceeds the band gap energy, electrons move from the valence band to the conduction band and lead to the generation of positively charged holes in the valence band [146-148]. These photogenerated charge carriers initiate a series of redox reactions at the catalyst surface that lead to the degradation or mineralization of the organic pollutant [149-150]. The photogenerated holes act as a strong oxidizing agent that can directly oxidize adsorbed organic molecules or react with the water molecules present on the surface or with the hydroxide ions that will produce the highly reactive hydroxyl radicals ($\cdot\text{OH}$). Similarly, the excited electrons in the conduction band participate in the reduction reactions where dissolved oxygen is reduced to form superoxide radical anions ($\cdot\text{O}_2^-$). This can further generate the hydroperoxyl radicals ($\cdot\text{HO}_2$) and hydrogen peroxide (H_2O_2) [149-151]. These reactive oxygen species cause a combined action on the dye molecule, which can follow different pathways like chromophore breaking, aromatic ring opening and oxidation of intermediate fragments [152]. Degradation occurs in the series of reactions by which it is ultimately mineralized into smaller molecular compounds, such as gaseous CO_2 and H_2O , and inorganic ions [149-150]. The photocatalytic pathways are discussed below and illustrated schematically in Figure 5:





The photocatalytic performance is dominated by the charge production and recombination of charges. The photocatalytic activity drops sharply when the electron-hole pair recombine too quickly. The reaction kinetics are highly dependent on factors like light wavelength and intensity, band gap energy, surface area, adsorption affinity of the dye, presence of an electron acceptor, pH and catalyst treatment such as metal doping or formation of heterojunction [151], [153-154]. In dye-contaminated wastewater, dye molecule generally adsorbs onto the photocatalyst surface before photodegradation occurs, and so interactions at the catalyst surface are believed to be an important step in the overall mechanism [155-156]. This mechanism framework is widely applicable to semiconductor-based photocatalysts and gives the basis for understanding photocatalytic degradation of both ionic and non-ionic dyes in aqueous systems[157].

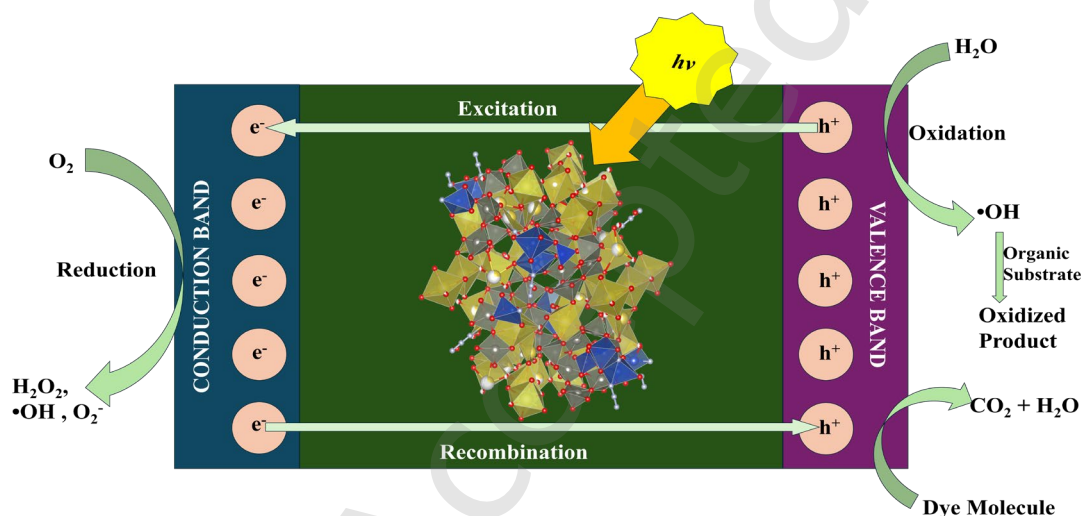
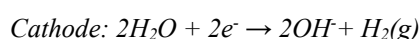
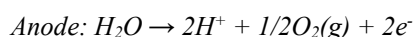


Figure 5: Schematic illustration showing the photocatalytic degradation mechanism of dyes and organic substrates using Polyoxometalate.

3.3. Photoelectrochemical process:

Polyoxometalates facilitate the photo-induced electron transfer, which generates Reactive Oxygen Species (ROS) that help in the degradation of dyes [158]. The process involves UV light, which excites the polyoxometalate and leads to electron transfer reactions [142]. Application of an external electric field via electrodes separates charge carriers and reduces recombination rates, which increases the degradation rate of dyes [159]. Photo electrocatalysis combines both photocatalysis and electrocatalysis to enhance dye degradation. The metal clusters support the charge separation and formation of Reactive Oxygen species (ROS) by acting as the redox active electron mediator and catalyst [160-161]. These polyoxometalates absorb UV/visible light depending on their constituents and metal ligands. Transition metal-substituted POMs (Cu, Fe, Co, etc.) show excellent catalytic activity in the degradation of dyes [67],[162-164].

In the electrochemical mechanism, first photo excitation occurs where POM or POM- modified electrodes are excited under light irradiation [165]. Then electricity is passed through the system. The photogenerated electrons move towards cathode and holes remain on the anode or the POM surface. This reduces the electron-hole recombination. The photogenerated electrons reduce the dissolved O_2 to superoxide $\cdot O_2^-$, which later forms hydroxyl ion ($\cdot OH$) or hydrogen peroxide (H_2O_2). Holes oxidize the water or hydroxyl ion (OH^-) to hydroxyl radical ($\cdot OH$), which is very reactive [166-167]. These reactive species ($\cdot OH$, O_2^- , h^+) actively react with the dye molecule and result in cleavage of bonds and ultimately destroy the chromophore group or the conjugation within the dye molecule. With stepwise oxidation, the dye molecule breaks down into smaller intermediates like CO_2 , H_2O and inorganic ions [168-169]. Continuous application of both electric field and UV light leads to the formation of hydroxyl ions ($\cdot OH$) near the cathode and promotes dye degradation. A schematic diagram of Photoelectrocatalytic dye degradation process using polyoxometalates is shown in Figure 6. Argote-Fuentes *et al.* [159] reported the photoelectron catalytic degradation of Congo red dye using activated hydrotalcites in the presence of a copper anode. The electrolysis reactions, as described by Argote-Fuentes, are mentioned below, and these occur simultaneously with the reactions mentioned under the photocatalytic mechanism above.



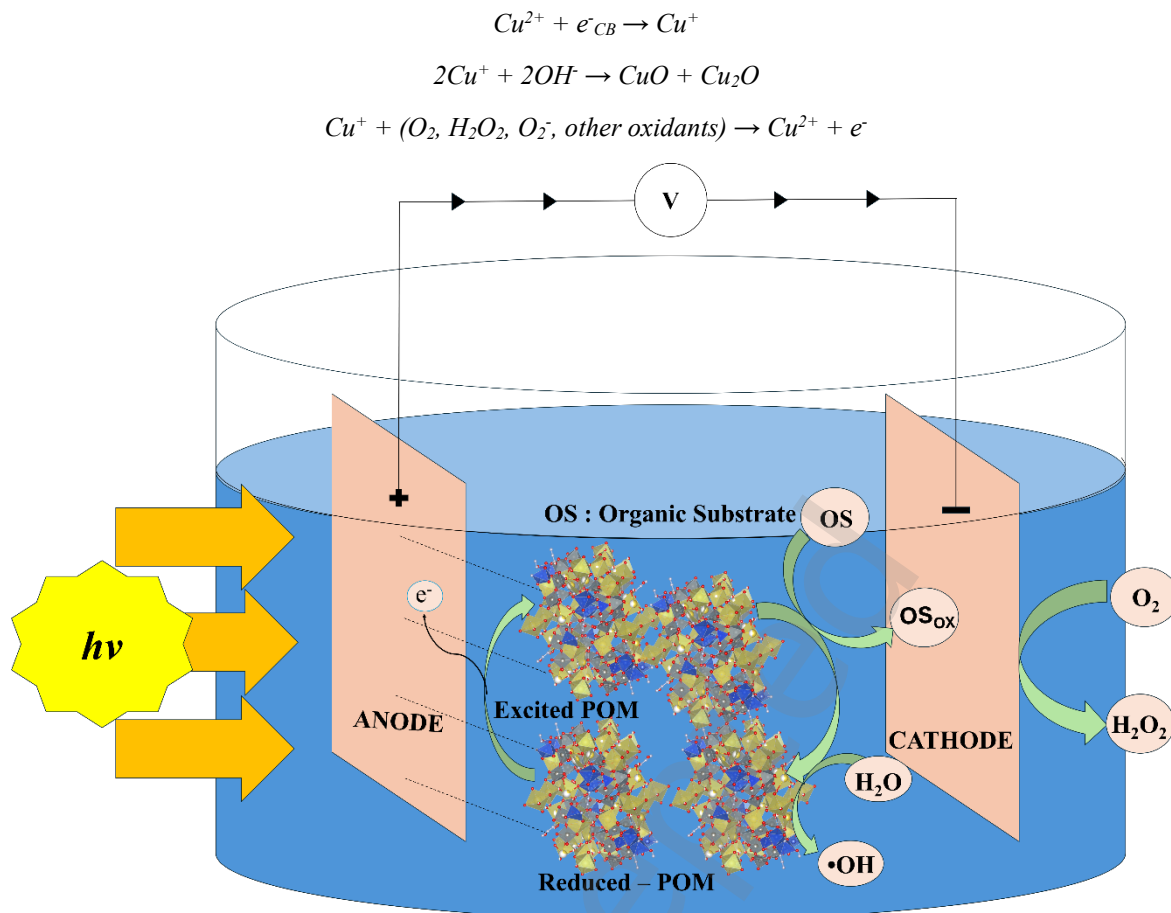


Figure 6: Schematic of Photo-electrocatalytic dye degradation process using polyoxometalate.

3.4. Fenton-like reaction:

In polyoxometalate-based Fenton-like reactions, hydrogen peroxide (H_2O_2) acts as an oxidizing agent and POMs as a catalyst. Here, iron is stabilized inside the structure of the catalyst. The reaction starts with the addition of H_2O_2 to the solution, which initiates the redox interactions that lead to the formation of hydroxyl radicals. These oxidative species play an important role in the degradation of organic pollutants through the oxidation process. These Fenton-like reactions rely on the generation of a catalytic radical to achieve efficient oxidation of a broad range of organic pollutants [170-171]. A schematic illustration Fenton Mechanism for dye degradation carried out by POMs is shown in Figure 7.

In the Fe-POM structure, iron exists as Fe (III). Usually in Fenton reactions, there is redox cycling of Fe (III)/Fe (II) and Fe^{3+}/Fe^{2+} by H_2O_2 . Here, Fe (II) reacts with H_2O_2 to form hydroxyl radical ($\cdot OH$) and convert to Fe (III). Later, Fe (III) is reduced to Fe (II) and allows the cycle to continue. The conversion of Fe (II) from Fe (III) is the rate-limiting step due to a lower rate constant (0.001-0.01 M⁻¹s⁻¹), suggesting the efficiency of the Fenton reaction. During this step, H_2O_2 is degraded to hydrogen peroxide radicals ($\cdot HO_2$), which are involved in the degradation of pollutants [172].

POMs show high catalytic activity for dye degradation when used in a Fenton-like reaction. A study show when Fe-containing POMs are coupled with defect-rearranged TiO_2 , then it shows comparatively higher degradation of toxic chemical dyes (sulfosalicylic acid (SSA) and bisphenol A) than normal TiO_2 [170]. In another study, a hybrid catalyst Co-POM/N- TiO_2 was tested for the degradation of Rhodamine-B under visible light and achieved 97.47% degradation rate within 40 minutes at neutral pH. Here, instead of Iron (Fe), Cobalt (Co) is used to initiate the Fenton reaction with H_2O_2 [173]. POM have several advantages, like a broader working pH range and the elimination of iron sludge formation that usually forms in traditional iron-based catalysis. This makes them suitable for multiple cycles of use without loss of activity [174-175]. Although it has been witnessed that the POM catalysed the Fenton Reaction, which is effective for the degradation of the pollutants, the generation of $\cdot OH$ radicals has raised concern regarding potential toxicity to both humans and aquatic biota in many different ways [176].

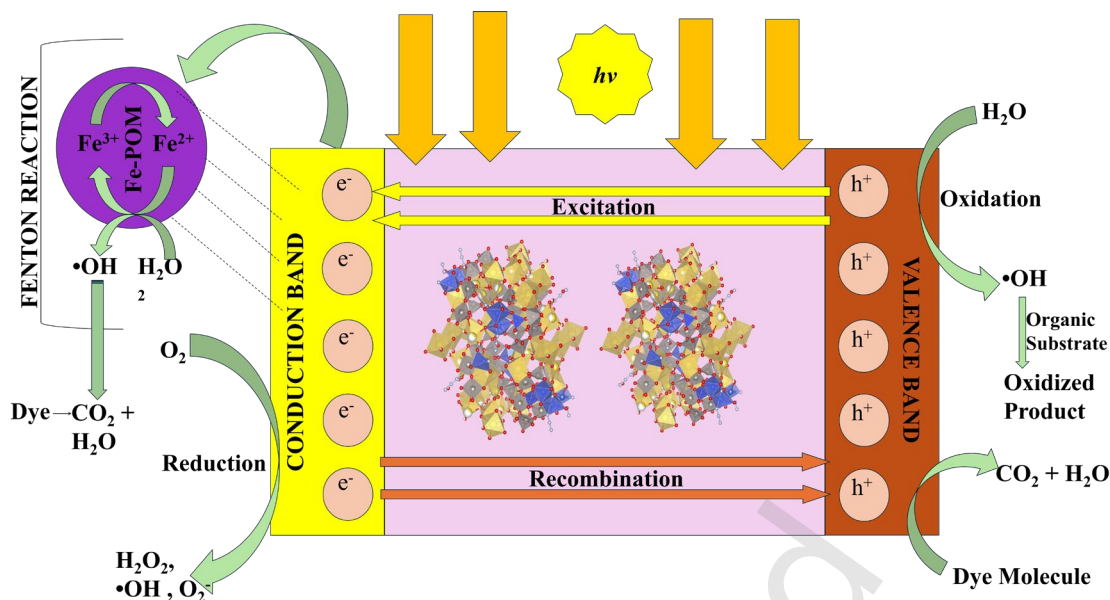


Figure 7: Schematic illustration of the mechanism involved in Fenton Reactions carried out by Polyoxometalate.

4. Factors affecting dye degradation

4.1. pH:

The degradation ability of POMs is mostly pH dependent. For example, degradation of methyl orange using $\text{Na}_2\text{W}_6\text{O}_{19}$ (a Lindquist POM) is effective in the presence of UV light at acidic pH. Similarly, the degradation of methylene blue (MB) using $\text{Ag}_4\text{PW}_{11}\text{VO}_{40}$ (a Keggin POM) is also highly effective in acidic pH [62]. The polyoxometalate CoV-POMs/PMS system showed a significant decrease in degradation efficiency from 93.3% to 41.12% when the pH was increased from 7 to 11 [92]. Other studies have shown that acidic conditions usually enhance the degradation rates [177].

In alkaline pH, the positive charge in the solution decreases, and the adsorbent surface becomes more negatively charged. As a result, cationic dye adsorption is favoured while anionic dye uptake decreases. Similarly, in an acidic medium, the positive charge in the solution increases, and the adsorbent becomes positively charged. As a result, anionic dye adsorption is favoured, and uptake of cationic is reduced [178-180].

4.2. Initial concentration of dye and adsorbent:

The initial concentration of dye plays an important role in determining the number of dye molecules that are present for the available adsorption sites. When the concentration is low, more active sites are available, and higher efficiency is observed. At higher dye concentrations, the fixed number of adsorption sites becomes less, leading to a gradual decrease in percentage dye removal. Similarly, a higher adsorbent dosage generally leads to great dye removal efficiency, as the addition of more adsorbent increases the number of available surface sites. This increases the dye uptake, resulting in a higher percentage of dye removal in the solution [181-183]. Studying the influence of adsorbent dosage provides information about how effectively a dye can be removed using the lowest possible amount of adsorbent, which is a key consideration when looking from the economical viewpoint [181]. For example, a study discusses the effect of the catalyst Co-POM and dye concentration in the degradation of indigo carmine (IC) and methylene orange (MO) dye [162]. The study shows similar results as explained earlier in the section.

4.3. Effect of temperature:

Variation in adsorption capacity with change in temperature gives important information about the adsorption process, i.e., whether the adsorption is endothermic or exothermic. If temperature increase results in high uptake of dye, then the process is endothermic. This can be associated with enhanced dye mobility and increased availability of active sites on the adsorbent surface [184]. However, too high temperature can have a negative effect on the adsorption as too high temperature can lead to destabilizing the polyoxometalate structure and catalyst deactivation. Additionally, too high temperatures may reduce dye adsorption on the catalyst surface due to weakened electrostatic interactions. This will negatively affect the overall dye removal efficiency [185].

5. Use of POM@MOF for dye degradation

Metal organic frameworks (MOFs) are crystalline porous materials where metal nodes are joined to organic linkers, leading to the formation of 3D coordination structures [186]. In POM-MOF material, metal oxide nano clusters are linked to organic frameworks. They show structurally diverse materials with high potential that are not limited to catalysis, separation and energy storage [187]. For example, recent studies show it is possible to use POMs with various MOFs in the formation of polyoxometalate-based MOFs (PMOFs), where PMOFs also have many unique properties covering both POMs and MOFs in one system that has excellent photocatalytic and photo thermal abilities [188-189].

POM-MOF hybrid can be used as an effective adsorbent for a variety of pollutants such as heavy metals and organic compounds. For example, a 2022 study, Lan *et al.* prepared $\text{PMo}_{10}\text{V}_2\text{O}_{40}@\text{MIL-101}$, showed a very large adsorption capacity of 912.5mg/g for tetracycline, a type of antibiotic, which is much higher than that of activated carbon [190]. The removal of dyes and Cr (VI), which

is proven to be the most dangerous and omnipresent metal environmental pollutant, is imperative [191]. Immobilization of POMs inside the MOF contributes to less leaching and aggregation of active sites that results in enhanced structural stability, recycle and reusability of the catalyst for industrial wastewater treatment [192]. MOFs have a naturally porous framework with a large surface area, which is important for efficient dye adsorption. The structural advantages combined with the redox activity of POMs support much better degradation efficiency [193-194]. The composite of POMs with MOFs are potential for water treatment because of its intrinsic properties [195]. Because of their superior electronic properties, POMs possess a great photocatalytic activity that could be applied for organic pollutant degradation in presence of visible light [196]. The synergistic effect between POMs and MOFs is favourable for both the adsorption and photodegradation processes [197]. These composites represent a new class formed via integration of POM clusters within the metal-organic framework. The primary merit of unification lies in the mutual stabilization within the single synergistic framework [192]. For example, POM-based MOFs have better photocatalytic activity and recycling performance for degradation of cationic dyes, i.e., Methylene Blue (MB) and Rhodamine-B (RhB) [189], [197].

A recent study, Royan *et al.*, 2025, discussed a PTA-modified $\text{NH}_2\text{-MIL-88B(Fe)}$, a POM@MOF, that has excellent cationic dye adsorption capacity of 95.7% in 2 minutes [183]. Similar other studies focusing on dye removal also showed POM@MOF systems with high dye removal efficiency. For example, $\text{AuW}_{12}\text{O}_{40}\text{@HKUST}$ showed 95% of dye color removal in 30 minutes [198]. $\text{Mn-BTC@Ag}_5[\text{BW}_{12}\text{O}_{40}]$ showed Rhodamine B (RhB), Methyl orange, and methylene blue dye degradation efficiency exceeding 90 % in 140 minutes [199]. $\text{SiW}_9\text{V}_3\text{@MIL-101(Cr)}$ showed high dye removal efficiency for Methylene Blue and Rhodamine-B dye [200]. $\text{P}_2\text{Mo}_{18}\text{/MIL-101(Cr)}$, showed 100% removal of methylene blue in 3 minutes and 99% for Rhodamine-B but was negligible for methyl orange [201]. In 2025, Sun *et al.*, discussed $\text{TiO}_2\text{@polyoxometalate-organic framework}$, where TiO_2 is added in $\{[\text{Ni}_6(\text{OH})_3(\text{H}_2\text{O})_5(\text{PW}_9\text{O}_{34})] (1,2,4\text{-Hbtc})\} \cdot \text{H}_2\text{enMe} \cdot 5\text{H}_2\text{O}$. The composite, $\text{TiO}_2\text{@Ni}_6\text{-POMOF}$, showed high dye removal efficiency for Methylene Blue and Rhodamine-B [202]. These studies provide a new and promising ground for the development of POM@MOF catalyst in future.

5.1. Parameters governing POM@MOF formation

In MOFs, the transition metal ions are commonly coupled with hydroxide, oxide, water and carboxylate ligands to shape divergent POM nodes which contribute significantly to intensifying the structural stability of the framework [203]. The large cavities present in the MOF are of suitable dimensions to cocoon relatively bulky clusters such as POMs. However, some specific requisites need to be met for synthesizing the POM@MOF composites, and these are:-

- Befitting-sized cavities to sheath the POMs [204].
- Compatible pH value for both MOFs and POMs [205].
- Homogeneous reaction conditions, i.e. the solubility of POMs, MOFs and the ligand should be matched [206].

Most of the POMs are stable in strongly acidic media, but there are only limited MOFs that have sufficient chemical validity to withstand the acidic medium [207]. Zirconium-based MOFs such as UiO-series and NU-type frameworks are among the most acid-tolerant, and this is attributed to the presence of strong Zr-O bonds formed via hard acid-hard base interactions [208-209]. These MOFs maintain structural uprightness at pH values as low as 1 and render large, well-defined pockets suitable for encapsulation of Keggin, Dawson, and lacunary POMs [210]. Chromium-based MOFs, explicitly the members of the MIL family, MIL-101(Cr) and MIL-100 (Cr), also exhibit magnificent firmness under acidic hydrothermal conditions and hold exceptionally large mesoporous cages, making them a supreme host for massive POM species [211-212]. Additionally, the POM@MOF composites, in which the MOFs embody porphyrinic linkers, are also engaging in heterogeneous catalysis [213]. On the contrary, most Zn- and Cu-based MOFs endure framework decomposition under such acidic conditions and hence are ill-suited for the POM fusion [214].

5.2. Incorporation of Polyoxometalates into Metal-Organic Frameworks

Metal-organic frameworks (MOFs) are widely used as host matrices for incorporating guest species due to their high internal surface areas, adjustable porosity, and ordered pore structures [215]. Various catalytically active components, including metal nanoparticles [216], proteins [217], and POMs [218], have been successfully immobilized within MOF pores. In 2005, Férey *et al.* reported the first POM@MOF composite by encapsulating the Keggin-type POM $\text{K}_7\text{PW}_{11}\text{O}_{39}$ into the large mesoporous cages of the chromium-based MOF MIL-101 using a post-synthetic impregnation method [218]. Since then, a variety of thermally and chemically stable MOFs, including UiO [219], MIL [220], ZIF [221], and NU-1000 [222], have been explored as supports for POM confinement in catalytic systems. In 2010, Gascon *et al.* reported the synthesis of $\text{PW}_{12}\text{@MIL-101}$ composite, $[\text{PW}_{12}\text{O}_{40}]^{3-}$, via one-pot synthesis and wet impregnation method [223]. A comparable detailed study was performed by Canioni *et al.* for encapsulating $\text{PMo}_{12}[\text{PMo}_{12}\text{O}_{40}]^{3-}$ in MIL-100(Fe) [224]. The one-pot solvothermal synthesis achieved POM loadings close to the theoretical maximum and produced composites with excellent aqueous stability, showing no detectable POM leaching even after two months. Conversely, materials made by impregnation exhibited significant POM leaching over the same timeframe [224]. One-pot synthesis, although not suitable for all MOF systems, offers benefits such as better POM retention [225], improved framework crystallinity [226], and reduced leaching [225], especially when the POM size exceeds the MOF pore aperture. Importantly, incorporating POMs by either method generally enhances the thermal stability of the original MOF framework [227-228]. Figure 8 illustrates a general incorporation of POMs into MOFs.

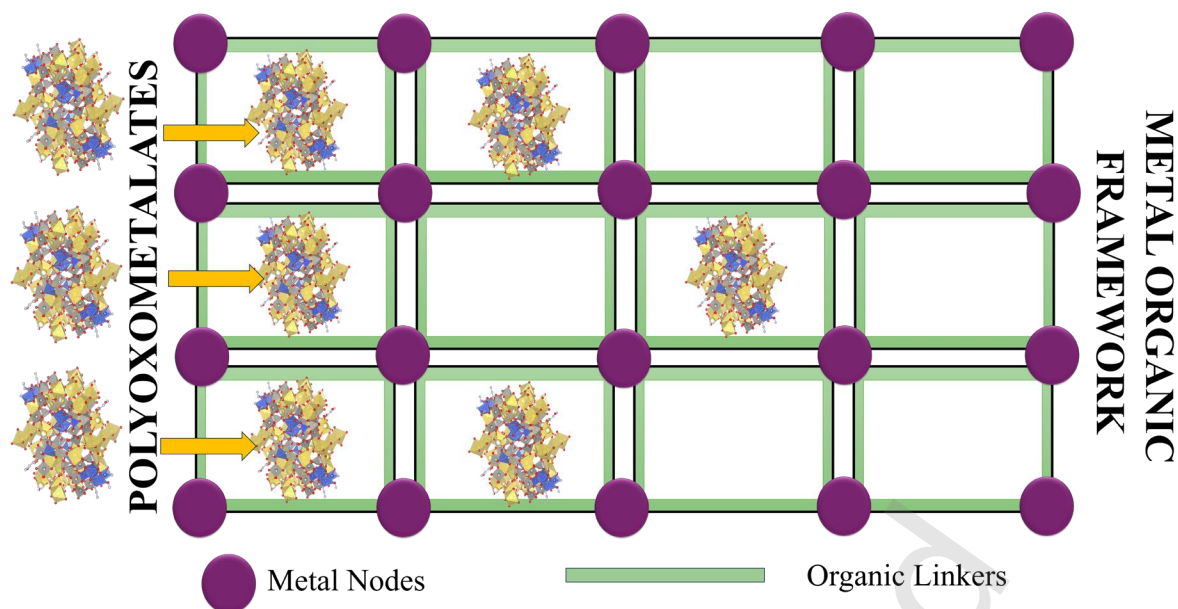


Figure 8: Incorporation of Polyoxometalates into Metal-Organic Frameworks

6. POM@TiO₂ Systems:

POM@TiO₂ systems are highly effective photocatalysts for dye degradation, primarily due to their ability to prolong the lifetime of the photogenerated electron-hole pair. The addition of POMs into TiO₂ improves charge separation and slows the synergistic effect, thus increasing the photocatalytic efficiency compared to pure TiO₂ [229]. POMs here acts as electrophiles, attracting electrons from the conduction band of TiO₂, thereby hindering the faster synergistic effect of the electron hole pair within TiO₂. This charge separation mechanism leads to higher concentration of available charge carriers for redox reactions, thus increasing the photocatalytic efficiency [160]. Time-Resolved Microwave Conductivity (TRMC) is the primary analytical tool for the characterization of kinetics of photogenerated electrons, such as their lifetime and recombination pathways. TRMC measurements on POM@TiO₂ composites have shown kinetics that are significantly different from the TiO₂. This happens due to trapping of electron at the POM-TiO₂ interface and where it contributes to charge stabilization [230].

7. Adsorption isotherm:

The interaction between dye molecule and polyoxometalate surface or polyoxometalate catalyst before and after the dye removal is studied by adsorption isotherm investigation. Understanding the adsorption behaviour is important to interpret dye removal efficiency as it is the first step that starts the dye removal from the wastewater as here dye molecule start to interact with the polyoxometalate or catalyst surface. Depending on the dye structure [231], catalyst surface charge [232] and reaction conditions [233], polyoxometalates and their composites react with the dye molecule with electrostatic interactions [234-235], hydrogen bonding [236], π - π interactions [237] and also the coordination interactions [238].

Dye adsorption by polyoxometalate material is generally explained by the Langmuir model isotherm and Freundlich model isotherm. Langmuir isotherm is mostly used for polyoxometalates and their composites with homogeneous active sites. It assumes the catalyst as one single layer homogeneous surface with finite adsorption sites. The Freundlich model is mostly used for Polyoxometalates supported by metal oxides, carbon materials, clays, or polymers, as it explains the adsorption on heterogeneous surfaces and assumes that the adsorption process is governed by the concentration of dye molecules at equilibrium [239-241].

8. Adsorption kinetics:

The rate at which dye molecules are adsorbed by the polyoxometalates and their composites is described by adsorption kinetics. Adsorption kinetics also explains the mechanism that governs the adsorption process. Kinetic study is important as the rate of adsorption is directly affected by the concentration of dye and adsorbent. Diffusion resistance [242], porosity [243], surface functional groups [233] and the type of dye catalyst interactions affects the adsorption kinetics in polyoxometalate system. The adsorption behaviour of dye POM system is mainly studied using pseudo first order kinetic model and pseudo second order kinetic model. First one is mainly connected to physical adsorption processes and Pseudo second order kinetic model explains about the chemisorption involving electron sharing redox active sites of the polyoxometalate material and the dye molecule [200].

9. Desorption study:

It is needed to check the reversibility of the dye adsorption on the polyoxometalate (POMs) as well as to understand the catalyst stability and reusability throughout numerous degradation cycles. Desorption is required to remove degradation intermediates and products to maintain catalytic activity [200]. Desorption experiments are essential for understanding the nature of adsorption processes, particularly in distinguishing between reversible and irreversible adsorption. These experiments often involve the use of suitable eluents or modification in pH or ionic strength to support desorption [244-246]. Desorption gives a clear explanation of dye-polyoxometalate interaction and supports the analysis of the adsorption isotherm and kinetic study. In wastewater treatment applications, these studies are important for maximizing the catalyst design, enhancing recyclability and attaining effective and sustainable dye degradation [246].

10. Future Outlook:

Future research on POMs should move beyond isolated catalytic activity and explore their multifunctional abilities, particularly their ability to simultaneously adsorb and degrade multiple classes of dyes present in real textile effluents. Expanding the structural chemistry of POMs by incorporating underexplored heteroatoms beyond the commonly studied phosphorus heteroatom, p-block elements could provide access to new electronic properties and reactivity patterns, thereby enhancing dye-POM interactions. Additionally, systematic investigation of indigo dye degradation using POMs is strongly needed, given the extensive industrial use of indigo in denim manufacturing and its significant discharge during washing processes. Addressing these gaps may improve the practical applicability of POM and POM-based materials for textile wastewater treatment.

One of the major issues with the application of polyoxometalates based catalysts for industrial applications includes catalyst leaching and heavy metal toxicity. Many strategies like immobilization or incorporation of POMs in MOFs, cage linkers, hollow nanoparticles are currently under exploration. Some studies also suggest the use of less toxic metals, such as Mn, Co and Cu, as alternative to conventional employed metals. To ensure the safe and sustainable use of POM-based catalysts, standardizing leaching assessments using techniques like ICP-MS, along with life cycle assessments (LCA), are recommended. The long term vision of POM based environmentally friendly catalysts should focus on achieving Sustainability, Recyclability, Scalability and Non-Toxicity as schematically represented in Figure 9.

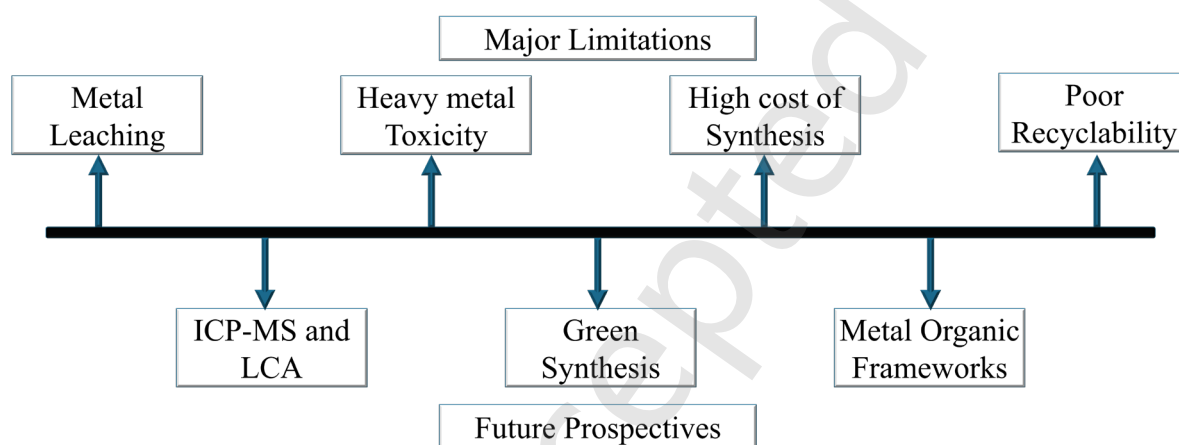


Figure 9: Schematic Representation of current limitations and future prospectives.

Regardless of their crucial potentiality for future waste water treatment technologies, bimetallic POM catalysts limit their practical applications in AOPs (Advanced Oxidation Processes). The bimetallic POMs should be unified with advanced auxiliary resources such as graphene derivatives, biochar, metal-organic frameworks, unexplored acidic MCM type 3D porous material and magnetic composites to intensify the perpetuity of the catalyst and to downplay lixiviating. A plenty of AOP configurations depend on UV sources for irradiation or high intake oxidants which ultimately raise the operational costs and restricts the viability of bimetallic catalysts in an environment of limited resources. Thus, in order to mitigate the operational fuel penalty, visible-light-driven AOPs and hybrid renewable energy systems (HRES), should rather be capitalized. Strategic Foresight should focus more on integrating computational modelling with scientific researches to foster the rational blueprint of the catalyst. Ecotoxicological investigations and Zebrafish analysis have suggested that prolonged disclosure to partially degraded dye can root for congenital malformations, while phytotoxicity examinations highlight that exposure to intermediate metabolites can drop the germination and growth rate in plants. Therefore, the future findings should underline the importance of assessing both metal-mediated - catalyst release and metabolite toxicity while nominating AOP setups for waste water treatment.

Data Availability

Not Applicable.

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Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

Author Contribution Statement

R.S.: Writing - original draft, visualization, conceptualization. B.K.: Writing - original draft, conceptualization. R.L.: Writing - original draft, Validation. M.K.S.: Validation, conceptualization. F.H.: Writing – original draft, review and editing, supervision, conceptualization. All authors have approved the final manuscript.

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