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Review

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Application of polyoxometalates and their composites for the degradation of antibiotics in water medium

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Abstract

This paper summarizes the potential of polyoxometalate (POM)-based catalysts in view of pharmaceutical wastewater treatment and recent advances that took place in this field. POMs are anionic clusters of transition metals, which exhibit unique characteristics such as high catalytic activity and multi-electron redox properties. Recently, they have been explored by some research groups for degrading antibiotics and pharmaceutical compounds (PCs) from contaminated water matrix. Several modifications of POM, along with their composite formation with new-age materials like g-C_3N_4 and reduced graphene oxide (RGO), have led to the formation of novel photocatalysts, which have also been reported as active materials to destroy the PCs. These promising catalysts have revealed the efficiency of complete destruction of these recalcitrant compounds within a short reaction time and showed good reusability characteristics. Among the widely used PCs, the notable ones include tetracycline (TC), sulfamethoxazole (SMX), ciprofloxacin (CIP), *etc.* Most of the articles cited here centered on TC degradation followed by other drugs. The effects of different operating conditions, degradation efficiency, and mechanism and stability aspects of various POM-based catalysts are discussed. The current knowledge gap in this area with bright future perspectives is also highlighted. The description will provide valuable insight to the research

community regarding the capability of POM-based catalysts to eliminate antibiotics, as well as designing highly efficient catalysts for a sustainable future.

Keywords: Antibiotics, degradation, polyoxometalates, photocatalysts, tetracycline

INTRODUCTION

With the shining advancement of medical science, the current world witnesses an uprising of a plethora of new-age drugs and pharmaceutical compounds (PCs), which are often utilized to combat different kinds of diseases in order to protect human lives. Obviously, usage of these updated PCs[1] helps in developing immunities against diversified categories of diseases. As a result, life expectancy is also enhanced. So, the natural outcome of this development is the huge demand for PCs and antibiotics globally. In particular, the COVID and post-COVID period witnessed a huge surge in drugs and antibiotic consumption[2] throughout the world. However, a recent review reports that the pharmaceutical industry consumes around 22% of the available freshwater for industrial purposes[3]. After manufacturing, a huge quantity of wastewater is generated from this unit containing residues of different antibiotics. These compounds are basically composed of organic molecules with a stable structure that is resistant to degradation under natural conditions. The prevalence of these recalcitrant compounds in the water bodies is undoubtedly a potential threat to overall ecosystems. The existence of PCs in water bodies obviously denotes hazard. For example, large quantity accumulation of tetracycline (TC) drug, a broad-spectrum antibiotic often used for fighting against several diseases, can lead to the development of drug-resistant genes[4]. The growth of these antibiotic-resistant genes (ARG) reduces the therapeutic potential to fight against pathogens. Apart from TCs, other antibiotics, such as macrolides, sulfonamides, fluoroquinolones, *etc.*, are also capable of producing ARG, and they are often spread among different microorganisms via a horizontal gene transfer mechanism[5]. Moreover, during the treatment of different categories of industrial wastewater, these compounds are often partially degraded, producing more toxic intermediates. Li *et al.* highlighted the important result obtained in this respect during the photocatalytic degradation of acyclovir applying g-C_3N_4/TiO_2 photocatalyst under visible light irradiation[6]. One of the intermediates produced, guanine, is almost three times toxic in comparison to the parent compound. Rizzo *et al.* also concluded a similar report[7]. Degradation of a wastewater treatment plant effluent containing mixtures of amoxicillin, carbamazepine, and diclofenac was carried out using a heterogeneous TiO_2-based catalyst. However, results indicate that complete degradation was not possible under the experimental condition.

Hence, due to several risks associated with the residual PCs in the water bodies, they have been marked as one of the notable emerging pollutants in the present industrial period. Environmental scientists and engineers are carrying out research activities to develop technologies for eradicating these compounds from water bodies. Conventional biological processes often fail due to the non-biodegradable nature of the antibiotics. Adsorption, catalysis, and membrane filtration, like advanced techniques, are often recommended by the research groups for the abatement of PCs. Adsorption is a versatile water treatment technique that is useful for a wide category of pollutants[8-10]. Different novel adsorbents have already been reported in the literature. Many promising ones are yet to be explored for the same. However, adsorption does not lead to the ultimate mineralization of the organic compounds, which is a severe demerit. Membrane filtration is a costly technique and may not be feasible for industrial usage on a large scale. Nevertheless, catalytic degradation can be regarded as a green technology for eliminating PCs. However, the development of a promising catalyst with good degradation and reusability is a challenging task for the research community. Many new-age materials have evolved as promising catalysts. Recently, we reviewed the efficiency and applicability of g-C_3N_4-based composite catalysts for the degradation of PCs[11]. The use of photocatalysis for cleaning water and sewage has been studied extensively[12]. Researchers have done a

significant amount of research over the past few decades on the development of a variety of semiconductors, including TiO_2[13] and ZnO[4], for their application in photocatalytic procedures. Very recently, polyoxometalates (POMs) have drawn the attention of scientists for pollutant degradation[14]. Yu *et al.* were successful in the synthesis of three distinct manganese POMs: $[Mn_3(H_2O)_3(AsW_9O_{33})_2]^{12-}$, $[Mn_3(H_2O)_5(PW_9O_{34})_2]^{9-}$, and $[Mn_3(H_2O)_3(SbW_9O_{33})_2]^{12-}$[15]. Among these three, $[Mn_3(H_2O)_3(SbW_9O_{33})_2]^{12-}$ was found to be superior compared to the other two in terms of the catalytic property for the oxidation of water. Neither manganese oxide nor Mn^{2+} (aq.) was discovered in the course of the photocatalytic oxidation of water. Cai and Hu studied the effects of light-emitting diode (LED) and ultraviolet A (UVA) radiation on the photocatalytic breakdown of sulfamethoxazole (SMX) and trimethoprim in a continuous photoreactor that contained TiO_2[16]. Irradiation for 20 min resulted in > 90% degradation of SMX and trimethoprim at an initial concentration of 400 ppb. In the research on the antimicrobial activities that took place during the photocatalytic procedure, a reference strain of *Escherichia coli* was also examined and tested. A concomitant reduction in residual activity against bacteria was observed for each dilution of trimethoprim that was eliminated.

POMs, which share a photocatalytic feature with conventional semiconductors, have recently been employed as efficient photocatalysts for the removal of organic compounds from polluted water. Clusters of three or more transition metal oxyanions that are bound together by the sharing of oxygen atoms make up POMs[17]. The metal atoms exist in higher oxidation states, and they belong to either group V or group VI of the transition elements. Molybdenum (VI), tungsten (VI), niobium (V), tantalum (V), and vanadium (V) are examples of transition metals [Figure 1] that can have unfilled d electron configuration[18]. Ammonium phosphomolybdate with the formula $(PMo_{12}O_{40})^{3-}$ and a Keggin-type structure was the first POM to be created in 1826 by Berzelius and further characterized in 1934. Other POMs were discovered after this invention[19]. For example, the phosphotungstate anion $[(PW_{12}O_{40})^{3-}]$ has a phosphate group at its core and is constructed from a framework that includes twelve octahedral tungsten oxyanions in the tungstate framework[20]. POMs are of considerable interest to scholars in a variety of subject areas, including the biological sciences, chemistry, molecular electronics, and materials science. This is due to the fact that POMs possess a variety of distinctive characteristics, including a high degree of tunability, oxidant features, and a high level of acidity. POMs have been employed as photocatalysts for the degradation of organic dyes[21] and pharmaceutical impurities[22]. In the recent past, ammonium phosphomolybdate was used by us as a photocatalyst for the hydroxylation of benzophenone[23]. Additionally, POMs have been used as photooxidation catalysts for the oxidation of a wide variety of organic compounds, including alcohols[24], olefins[25], and others. POMs find use in areas where their redox properties, photochemical action, ionic charge, and conductance are found advantageous. About 80%-85% of the published research papers on POMs relate to their usage as catalysts, while the remaining 15%-20% of papers discuss coatings, membranes, and thin films[26]. In reality, rising cancer rates and bacterial resistance to antimicrobials are two of the world's most pressing health issues. In addition, new medications to combat SARS-CoV-2 infection caused by the coronavirus are urgently needed in light of the current pandemic crisis. Many scientists are now interested in POMs[27-29] as potential replacements for traditional antiviral, antibacterial, and anticancer drugs. In this article, we summarize the findings of significant studies conducted in the twenty-first century on the environmental applications of POMs for the eradication of antibiotics such as TC, ciprofloxacin (CIP), SMX, and others. These studies investigate the stability of POMs as well as their future potential.

The aim of the current paper is to highlight the efficiencies of POM-based catalysts in degrading different PCs in an aqueous medium. Among the papers cited here, most of them have been published within the last five years. Most of the studies reported in the literature have been performed with TC. Hence, the degradation of TC and some other important drugs such as CIP and SMX, has been kept as the main focus

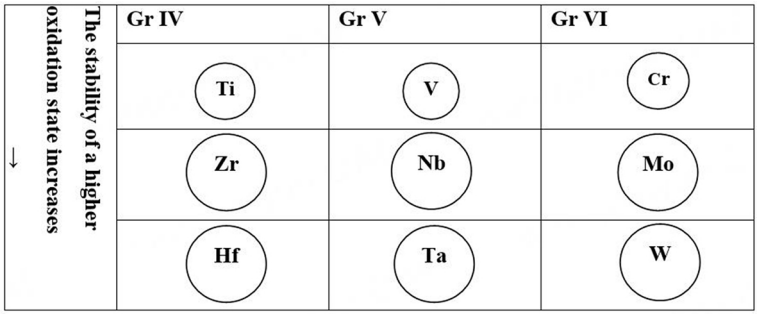

Figure 1. Change of oxidation states of transition metals.

of this article. The different mechanisms involved, the effects of operational parameters, and the current research gap in this area are described. Future perspectives have been put forward before concluding the article.

PREVALENCE OF ANTIBIOTICS AND CONTRIBUTING FACTORS TO ANTIBIOTIC RESISTANCE

Many reported studies in recent times showed the existence of PCs and antibiotics in natural water bodies and wastewater streams. They are released from the industrial units along with the discharged wastewater. Often, a large amount that is not metabolized inside the animal body is also released through urine in the environment. Hou *et al.* reported the concentration of TC, oxytetracycline (OTC), and chlortetracycline (CTC) in the treated effluent of a wastewater plant as 11.9, 334.3, and 1.8 mg/L, respectively[30]. Among several types of wastewater, these compounds are mostly prevalent in hospital wastewater. Hospital wastewater is a complex matrix consisting of analgesics, anesthetics, β-blockers, psychiatric, anti-inflammatories, *etc.* It is expected that in comparison to municipal wastewater, hospital wastewater possesses a 2-150 times higher concentration of PCs[31]. As a result of the huge discharge of PCs and their residues in the wastewater, they also reach the groundwater naturally via seepage. Hence, they are detected in groundwater in different parts of the world. Dai *et al.*, in one of their recent review articles, reported the occurrence of TC in shallow groundwater in China at a concentration of 184.2 ng/L[32]. Javid *et al.* also found traces of TC in surface and groundwater in some parts of Iran[33].

Antibiotics are widely utilized in the treatment of bacterial diseases in both humans and animals[34-36]. Even at extremely low concentrations, pharmacological formulations maintain their bioactivity and bioaccumulation. As a result, they permeate vital biological cycles and wreak havoc on the bodies of many different kinds of organisms, which ultimately develop immunity to antimicrobial treatments. Antibiotics degrade and self-degrade in vivo, producing more hazardous chemicals than the initial drug[37,38]. TC, CIP, and SMX are commonly used antibiotics that have become increasingly prevalent in bacterial strains. The widespread and inappropriate usage of these antibiotics has led to the development and emergence of antibiotic resistance mechanisms such as altered drug uptake, drug target alternation, and drug inactivation[39]. This has resulted in reduced susceptibility to these antimicrobial agents, rendering them ineffective in treating bacterial infections. The emergence and spread of antibiotic resistance mechanisms arise from complex interactions between numerous factors. Overuse and inappropriate usage of antibiotics in both human and veterinary medicine, as well as the inclusion of antibiotics in animal feed, have been identified as significant contributors to the increasing prevalence of resistance[40]. In addition to these factors, non-compliance with treatment, uncontrolled use of antibiotics, and unsanitary environments could also play a role in facilitating the development and spread of antibiotic resistance. The use of substandard

and counterfeit drugs, as well as the unauthorized sale of antibiotics without prescription in certain regions, further exacerbates this problem[41]. Figure 2 shows antibiotics and the factors that contribute to their presence throughout the entire ecosystem.

This issue is of utmost concern, as antibiotic resistance has the potential to cause devastating consequences both within healthcare systems and throughout society at large. It is associated with higher mortality rates, prolonged illness, and increased healthcare costs due to the need for additional diagnostic tests and antibiotic therapies. It is imperative that healthcare professionals, policymakers, and the public work together to combat antibiotic resistance through responsible use of antibiotics, promoting awareness of the issue, and supporting ongoing research into effective strategies for addressing this global threat. Furthermore, it is important to address the contribution of other factors such as disinfectant usage, as their effect on resistance prevalence can be difficult to evaluate but may represent a critical piece in the puzzle of combating this issue. Therefore, there is an urgent need to develop and implement comprehensive strategies that prioritize the appropriate use of antibiotics in human and veterinary medicine while also addressing the issue of counterfeit drugs and the unauthorized sale of antibiotics[42]. In addition to these measures, improved hygiene practices and surveillance systems, as well as the development of new effective antimicrobial agents, will be essential in combating antibiotic resistance and reducing its impact. Previous studies have revealed that the prevalence of antibiotics, including TC, CIP, and SMX, is significant in contributing to the development and spread of antibiotic resistance[43]. Addressing this complex issue will require a multifaceted approach that involves cooperation among healthcare professionals, policymakers, and the public. The emergence and prevalence of antibiotic resistance pose a serious threat that must be addressed with urgency. Failure to take action could result in catastrophic consequences for efforts to combat infectious diseases and public health more broadly. As such, minimizing the impact of antibiotic resistance requires a coordinated response that ensures the availability of effective antibiotics and vaccines and widespread access to rapid and reliable diagnostics.

POMS AGAINST DIFFERENT ANTIBIOTICS DEGRADATION

The photocatalytic degradation of antibiotics on semiconductor materials, particularly n-type semiconductors with suitable band gaps such as CdS[44-46], TiO_2[47-49], and ZnO[50-52], has shown great promise. These photocatalysts can efficiently convert solar energy into chemical energy and promote redox reactions[53-55]. However, it is common for electrons and holes to recombine, which results in a low level of photocatalytic activity[56-58]. POMs are a form of metal-oxygen anion nanocluster that is made up of plentiful oxygen atoms and highly oxidized early transition metals (such as Mo, Nb, Ta, V, and W)[59-63]. The process of precipitation is frequently used in the production of POMs. This method includes dissolving metal salts in a solvent (usually water) and then adjusting the pH level and temperature of the resulting mixture until it meets the required parameters[64-67]. The functionalization of pure inorganic POMs is important because it makes it possible to tailor the physical and chemical properties of POMs to specific requirements, hence opening the door to the development of further applications in the real-world environment.

The usefulness of POMs can be improved in three basic ways, e.g., (i) the solubility of POMs, which are normally negative charges, can be altered by exchanging their counter-ions with organic cations[68,69]; (ii) due to the high surface oxygen content of POMs, they can be used as inorganic ligands to coordinate with metal ions and construct high-dimensional coordinated complexes, which is made possible by their chemical structure[70,71]; (iii) POMs can be subjected to covalent modification with organic ligands, which paves the way for the rational development of inorganic-organic hybrid materials that are founded on POMs[72]. The extraordinary physicochemical properties of POMs, as well as their structural diversity and straightforward synthesis processes, can be of use in a wide variety of sectors, including photo- and electro-catalysis,

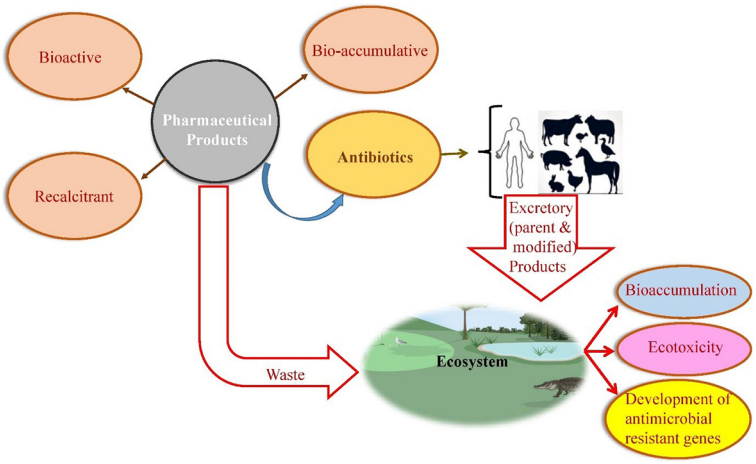

Figure 2. Antibiotics and their breakdown products are likely to travel and end up in a variety of ecosystems.

pharmaceuticals, magnetism, and energy storage and conversion, to name just a few of the many possible applications[73-76]. POMs, because of their semiconducting properties, have recently been demonstrated to be good candidates for the effective photocatalytic elimination of antibiotic pollutants[77-81].

Advantages of POMs

POMs have a structure that is analogous to that of semiconductors. Like semiconductors, POMs have a valence band (VB) that is filled with electrons and a conduction band (CB) that does not have any electrons in it. As can be seen in Figure 3A, the mechanism of photocatalysis utilized by POM catalysts is, in general, comparable to that of semiconductor catalysts. Photo-generated holes (h^+) and electrons (e^-) are created when the catalyst is bombarded with energy equivalent to or greater than its band gap, causing the electrons in the VB to be driven to the CB. In an environment comprised of water, the positive holes (h^+) will react with organic materials like pharmaceutical products to form hydroxyl radicals (·OH). Because of its powerful oxidizing capabilities, hydroxyl radical takes part as an active species in the process of oxidation and degradation of pharmaceutical products [Figure 3B][82]. Again, when photocatalytically active semiconductors like TiO_2 are put atop POMs, the photocatalytic activity of the POMs significantly increases[83]. In a circumstance like this, POMs will often act as scavengers, collecting the electrons that are produced when light passes through the semiconductor in order to form a reduced POM^- species. By doing so, we delay the recombination of h^+ and e^- pairs, which ultimately results in an increase in the efficiency with which hydroxyl radicals are created by h^+ from the semiconductor. In the meantime, the POM^- species oxidizes the pharmaceutical products by donating an electron to the dissolved oxygen in the solution. This creates superoxide ($\cdot O_2^-$) radicals, which react with water to produce hydroxyl radicals (·OH) and/or hydrogen peroxide (H_2O_2) molecules [Figure 3C][84]. Keggin-type POMs are frequently used in the photocatalytic destruction of emerging pharmaceutical contaminants because of their ideal band gap, high stability, and simple manufacturing. After modifying and loading to change the band gap, other types of POMs also have possible applications. POMs of different types also have the potential to be useful in a variety of applications after the band gap has been modified and loaded. There are a lot of positive aspects to employing POMs as photocatalysts, e.g.,

1. POMs include a high concentration of transition metals (including Mo, Nb, Ta, V, and W) and a large number of surface-accessible active sites.
2. The photocatalytic performance of POMs can be further enhanced by tuning the band gap in their structures. This can be accomplished by modifying the heteroatoms in their structures (such as P and Si) or

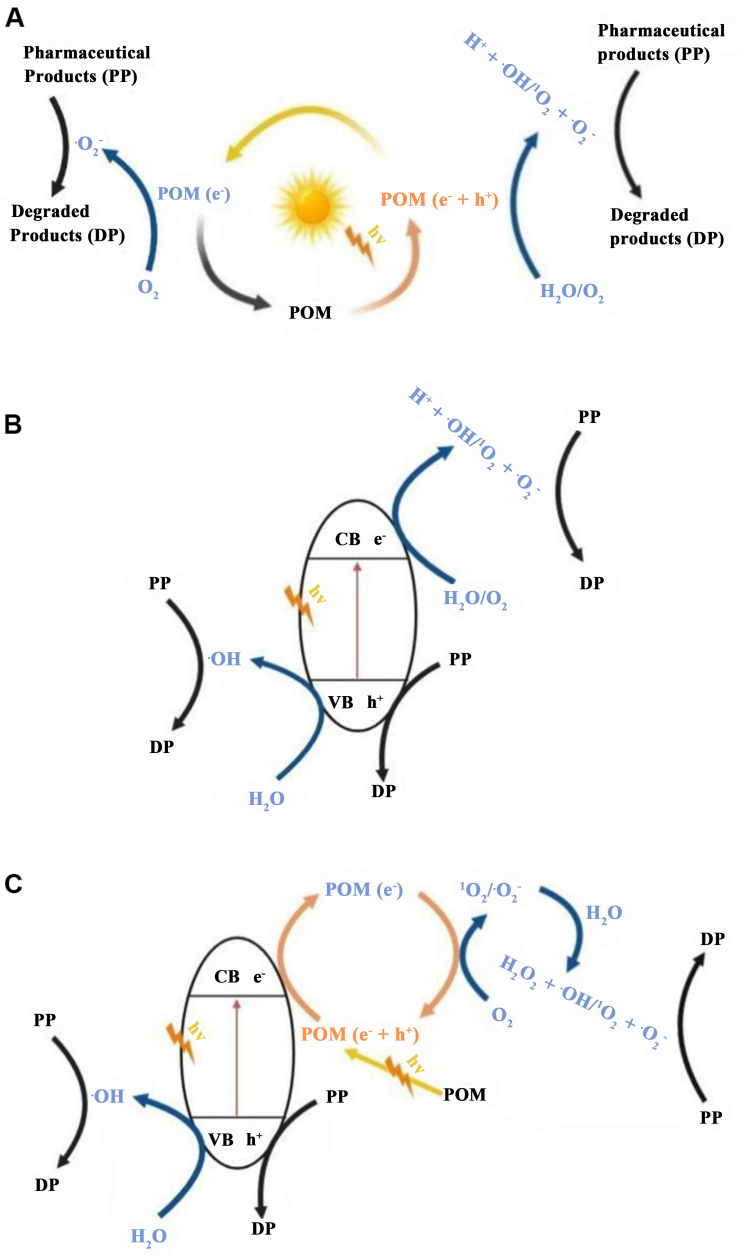

Figure 3. The photocatalytic mechanism of catalysts is represented in three different ways: (A) a diagrammatic photocatalytic scheme of POM-based catalysts; (B) the mechanism of pure semiconductor photocatalysts; and (C) the mechanism of POM-based composite photocatalysts. CB: Conduction band; POM: polyoxometalate; VB: valence band.

the valence states of metal atoms.

3. Matrix materials (such as carbon nanomaterials, TiO_2, and other support materials) and organic ligand-functionalized POMs can facilitate a synergistic impact between various constituents.

4. Single crystal X-ray diffraction provides a definitive molecular structure of POMs, which is useful for investigating the correlation between structure and function at the atomic level.

As a result, scientists are delving deeper into the design of the frames, photocatalytic character development, and analysis of the conversion methodology and kinematics of POM-based catalysts for the

photodecomposition of emerging pharmaceutical contaminants. Recent studies have shown that POM-based photocatalysts are highly effective at degrading antibiotics such as TC, CIP, and SMX.

Application of POMs and their composites in TC degradation

TCs represent a family of antibiotics, most of which are broad-spectrum drugs such as TC, doxycycline, minocycline, *etc.* However, sarecycline is a narrow-spectrum drug that is useful for treating acne, a dermatologic condition[85]. They are often prescribed to fight against bacterial infections of the skin, intestine, respiratory tract, *etc.* TC restricts the bacteria from producing proteins required for further growth. Hence, their spread and growth are prevented. The widespread use of antibiotics such as TCs has led to the presence of these substances in environmental matrices, including surface water and groundwater. Therefore, there is an urgent need to remediate antibiotic pollution through effective methods such as degradation. POMs and their composites have gained attention as potential candidates for the degradation of TC. Recent studies have suggested that POMs and their composites with g-C_3N_4 nanosheets, TiO_2, and polyoxotungstates (PW_{12}) exhibit great potential for the degradation of TC[86]. Moreover, POMs have shown effectiveness in degrading other antibiotics, such as sulfasalazine[87] and OTC[88]. Furthermore, the research has indicated that the efficiency of TC degradation can be influenced by various factors such as pH, temperature, light intensity, soil type, and composition. Organic carbon present in the environment may also have an effect on the degradation of TC due to its influence on adsorption and desorption equilibria. Therefore, the application of POMs and their composites in the degradation of TC presents a promising avenue for addressing the issue of antibiotic pollution in the environment. Chen *et al.* further demonstrated the potential of POMs and their composites in TC removal from water[89]. Their study utilized polyvinylpyrrolidone-modified nanoscale zero-valent iron prepared through the liquid-phase borohydride method for TC degradation. The findings of their research indicated that the POM-based composite exhibited excellent catalytic performance, with a degradation efficiency of up to 98.4% within 2 h.

In one of our recent works, microporous ammonium phosphomolybdate has been explored as the active catalyst for TC degradation purposes under ambient aerobic conditions[90]. The schematic is shown in Figure 4. With the initial concentration of TC being 20 mg/L, the dose of catalyst 0.75 g/L, almost complete degradation (~98%) took place within 90 min of reaction time. Detailed experimental investigation revealed that singlet oxygen and hydroxyl radicals played a major role in the degradation process. Further, it was observed that chemical oxygen demand (COD) removal was nearly 98%, while total organic carbon (TOC) removal was around 63.6% at the end of the reaction period. It indicates that intermediates formed during the catalytic oxidation were resistant to the mineralization process.

Many other POM-based novel catalysts of the recent era showed promising performance towards TC degradation in aqueous medium. Beni *et al.* reported the preparation of Au nanoparticles loaded POM/zeolite imidazolate nanocomposite as the active catalyst for TC degradation purposes[78]. The newly synthesized catalyst exhibited excellent performance in a wide pH range. However, at neutral pH, the removal efficiency was obtained highest. Shi *et al.* prepared composite material from $Cs_3PMo_{12}O_{40}$ and g-C_3N_4 to develop a highly efficient Z scheme photocatalyst for the removal of various recalcitrant pollutants from the water medium[79]. Under visible light exposure, 83.11% degradation was achieved in the case of tetracycline hydrochloride with a rate constant of 0.01255 min^{-1}.

In recent times, Sun *et al.* prepared a novel photocatalyst from a combination of phosphotungstic acid, Fe_2O_3, and carbon nanotubes by means of hydrothermal process and microwave irradiation[91]. The synergism between the Keggin structure of phosphotungstic acid and Fe_2O_3 made it a highly efficient catalyst for TC oxidation under visible light irradiation. Heng *et al.* used Lindqvist-type $K_7HNb_6O_{19}$ in

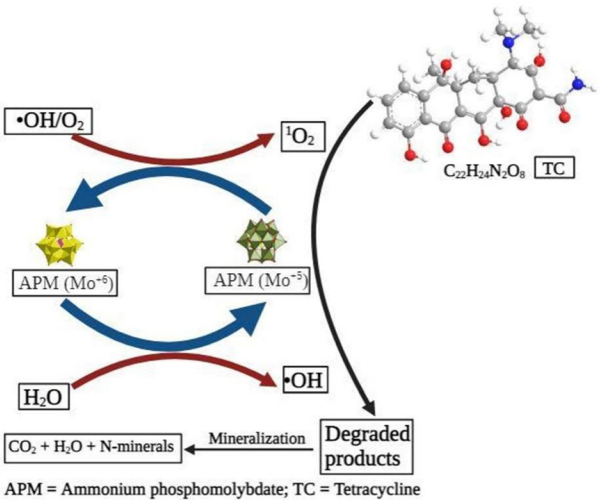

Figure 4. Schematic of TC degradation by application of microporous ammonium phosphomolybdate as catalyst.

different ratios with reduced graphene oxide (RGO) to synthesize a series of heterogeneous photocatalysts[92]. Among all the prepared catalysts, the one formed using 0.5 millimolar of $K_7HNb_6O_{19}$ showed excellent catalytic performance towards TC photodegradation, achieving removal efficiency of 74.69% in 9 min of reaction time. Yang *et al.* reported the promising application of Fe-POM/Bi_2MoO_6 composite catalyst towards TC degradation in a wide range of pH (3-11)[93]. The removal process proceeded via the photo-Fenton technique. Zhu *et al.* developed a composite catalyst from cobalt acetate, $H_4PMo_{11}VO_{40}$, and biochar to degrade different antibiotics in wastewater[94]. Degradation progressed in the presence of peroxymonosulfate (PMS). The catalyst was found to completely degrade TC in 30 min reaction time with a PMS concentration of 0.17 mM and a dose of catalyst as 0.15 g/L.

In conclusion, the application of POMs and their composites in TC degradation demonstrates promising results (as discussed in Table 1) for addressing antibiotic pollution in environmental matrices. The widespread use of antibiotics, specifically TC, has resulted in their presence in environmental matrices such as surface water and groundwater, and there is an urgent need to develop effective interventions for remediation. The use of POMs and their composites in antibiotic degradation presents an exciting prospect for solving the environmental contamination problem. The issue of antibiotic pollution in the environment has been a growing concern, particularly due to their widespread use.

As antibiotic residues can contribute to bacterial resistance, causing a serious risk to humans and other animals alike, new approaches, such as photocatalysis, have been explored to address such issues. The combination of POMs with nanoparticles has attracted significant attention due to the unique properties of this approach[106]. Various studies have reported the potential of POM-based composites in removing other commonly used antibiotics, such as SMX[81] and CIP[107,108]. These studies demonstrate the potential of POM-based composites to effectively reduce the concentration of antibiotics in environmental matrices, leading to a significant reduction in the risk of bacterial resistance and other adverse effects on human health and the environment.

Overall, the use of POM-based composites in antibiotic degradation represents a promising avenue for addressing the problem of antibiotic pollution in the environment. Further research is needed to optimize the performance of POM-based composites and evaluate their long-term effects on the environment.

Table 1. Summary of TC degradation studies by various POMs/POM-composites

POMs/POM-composites	Experimental conditions	Removal efficiency	Ref.
Multivalent supramolecular self-assembly between β-cyclodextrin derivatives and polyoxometalate (POM/EDA-CD)	At an initial concentration of TC 1 mM with 0.055 mM POM/0.03 mM EDA-CD = 3 mL, concentration of H_2O_2 = 50 μL (30% w/w), under irradiation of 50 W white mercury light irradiation	~100% in 25 min	[22]
Au nanoparticle-decorated polyoxometalate/Zeolitic Imidazolate Framework-8 nanostructure (ZIF-8@PTA@AuNP)	With an initial concentration of TC = 10 mg/L, dose of catalyst (ZIF-8@PTA@AuNP) = 0.5 g/L, under 125 W mercury UV light irradiation	97.0% in 60 min	[78]
Z-scheme $Cs_3PMo_{12}O_{40}$/g-C_3N_4 (x% CPM/CN)	At an initial concentration of TC = 20 mg/L, dose of catalyst (4% CPM/CN) = 0.40 g/L, under irradiation of visible light (λ_{max} = 420 nm)	83.11% in 120 min; 68.18% TOC removal in 120 min	[79]
Mesoporous TiO_2-doped with polyoxometalates $[PMo_{10}V_2O_{40}]^{5-}$ (PMV) and loaded with Ag nanoparticle composite (PMV-TiO_2/$Ag_{0.1}$)	At an initial concentration of TC = 20 mg/L, dose of catalyst (PMV-TiO_2/$Ag_{0.1}$) = 1.00 g/L, under irradiation of 300 W Xenon light (λ_{max} = 420 nm)	90.0% in 80 min	[84]
Microporous ammonium phosphomolybdate	Initial concentration of TC = 20 mg/L, dose of catalyst = 0.75 g/L, T = 303 K; pH = 4.1	~98% in 90 min; ~64% TOC removal in 90 min	[90]
Artificial chloroplast- phosphotungstic acid-iron oxide micro box heterojunctions penetrated by carbon nanotubes (HPW_x@Fe_2O_3-CNTs)	Initial concentration of TC = 10 mg/L, dose of catalyst (HPW_x@Fe_2O_3-CNTs = 0.25 g/L), under irradiation of 300 W Xenon light (λ_{max} = 420 nm)	100% in 100 min	[91]
2D polyoxoniobate/RGO (Nb-RGO-X; X is the mM amount of $K_7HNb_6O_{19}$)	Initial concentration of TC = 30 mg/L, dose of catalyst (Nb-RGO-0.5) = 0.40 g/L, under irradiation of UV light irradiation	74.69% in 9 min	[92]
Fe-polyoxometalate nanodots decorated Bi_2MoO_6 nanosheets (Fe-POM/BMO)	Initial concentration of TC = 20 mg/L, dose of catalyst (Fe-POM/BMO-3) = 0.40 g/L, concentration of H_2O_2 = 1.5 mM (30% w/w), under irradiation of 5 W white LED light irradiation of 73 mW/cm^2	99.79% in 18 min; 60.46% TOC removal in 18 min	[93]
Polyoxometalates supported on biochar (CoPMoV/C)	Initial concentration of TC = 20 mg/L, dose of catalyst (CoPMoV/C) = 0.15 g/L, concentration of PMS = 0.17 mM, under irradiation of 300 W Xenon light (λ_{max} = 420 nm)	100% in 30 min	[94]
Bi/Polyoxometalate doped TiO_2 (x% Bi/PT)	Initial concentration of TC = 20 mg/L, dose of catalyst (20% Bi/PT) = 1.00 g/L, under irradiation of 300 W Xenon light (λ_{max} = 420 nm)	86.0% in 60 min; 65.84% TOC removal in 60 min	[95]
Polythiophene Silverton-type polyoxometalate (x% PTh/Co_9W_{10})	Initial concentration of TC = 20 mg/L, dose of catalyst (PTh/Co_9W_{10}) = 1.00 g/L, under irradiation of 300 W Xenon light (λ_{max} = 420 nm)	74% in 120 min	[96]
Polyoxometalates into a metal-organic framework [MIL-101(Fe)]	Initial concentration of TC = 40 mg/L, dose of catalyst ($PMo_{10}V_2O_{40}$@MIL-101) = 0.04 g/L, under irradiation of 300 W Xenon light irradiation (λ_{max} = 420 nm)	~95% in 120 min	[97]
Polymer composite of phosphotungstic acid and polyaniline (PWA/PAN)	Initial concentration of TC = 25 μM, dose of catalyst (PWA/PAN) = 0.5 g/L, concentration of H_2O_2 = 50 mM (30% w/w)	100% in 30 min	[98]
Vanadium-substituted polyoxometalate doped magnetic carbon nitride (CoWV/mCN)	Initial concentration of TC = 10 mg/L, dose of catalyst (CoWV/mCN) = 0.5 g/L, under irradiation of 300 W Xenon light (λ_{max} = 420 nm)	82.4% in 120 min	[99]
Nanospherical α-Fe_2O_3 supported on 12-tungstosilicic acid (α-Fe_2O_3/12-TSA·7H_2O)	Initial concentration of TC = 30 mg/L, dose of catalyst (α-Fe_2O_3/12-TSA.7H_2O) = 0.15 g/L, concentration of H_2O_2 = 0.1 g/L (30% w/w), under irradiation of 15 W UV light (λ_{max} = 254 nm)	97.39% in 50 min	[100]
$K_5CoW_{12}O_{40}$/TiO_2 composite	Initial concentration of TC = 50 mg/L, dose of catalyst (30-$K_5CoW_{12}O_{40}$/TiO_2) = 5.00 g/L, under irradiation of 18 W fluorescent light	~100% in 120 min	[101]
Fe-polyoxometalates nanoparticles on porous and ultrathin g-C_3N_4 nanosheets with nitrogen vacancies (Fe-POM/CNNS-N_{vac})	Initial concentration of TC = 20 mg/L, dose of catalyst (45-Fe-POM/CNNS-N_{vac}) = 1.00 g/L, concentration of H_2O_2 = 10 mM (30% w/w), under irradiation of 300 W Xenon light irradiation (λ_{max} = 420 nm)	96.5% in 18 min; 78.5% TOC removal in 18 min	[102]
Polyoxometalate anchored zinc oxide nanocomposite (ZnO@PDA/Cu-POMs)	Initial concentration of TC = 50 mg/L, dose of catalyst (ZnO@PDA/Cu-POMs) = 50.00 g/L, under irradiation of 300 W Xenon light (λ_{max} = 420 nm)	90.75% in 90 min	[103]
Polyoxometalate intercalated La-doped NiFe-LDH	Initial concentration of TC = 5 mg/L, dose of catalyst	95.4% in 60 min	[104]

(NiFeLa{HPW}-LDH)	(NiFeLa{HPW}-LDH) = 0.10 g/L, concentration of PMS = 2.00 mM		
Flower-ball-like $ZnIn_2S_4$@hollow dodecahedral polyoxometalate ($K_3PW_{12}O_{40}$)@flower-shell-like $ZnIn_2S_4/Ag_2S$ yolk@shell (ZIS@HD-KPW@ZIS/AS)	Initial concentration of TC = 20 mg/L, dose of catalyst (ZIS@HD-KPW@ZIS/AS) = 0.20 g/L, under irradiation of 300 W xenon light (λ_{max} = 420 nm)	~99% in 120 min	[105]

EDA-CD: Ethylenediamine-β-cyclodextrin; LED: light-emitting diode; PMS: peroxymonosulfate; POM: polyoxometalate; RGO: reduced graphene oxide; TC: tetracycline; TOC: total organic carbon; UV: ultraviolet.

Additionally, factors such as pH, temperature, light intensity, soil type, and composition have been reported to affect the persistence of TC antibacterials[109]. Therefore, thorough consideration and management of these factors are necessary for the optimal performance of POM-based composites in tackling environmental antibiotic pollution. The issue of antibiotic pollution in the environment has been a growing concern, mainly due to the ubiquitous use of antibiotics such as TC. As a result, the implications of effective interventions for remediation cannot be overstated. Future studies should investigate the synergistic effect of POM-based composites with other remediation techniques such as activated carbon adsorption and bioremediation in order to develop comprehensive and sustainable approaches for managing antibiotic pollution in the environment. Furthermore, the development of innovative and sustainable antibiotic alternatives is crucial in reducing the widespread use of antibiotics that contribute to environmental pollution. The scientific community has also explored other approaches, such as photocatalysis, in addressing the issue of antibiotic pollution in the environment[37].

Application of POMs and their composites in CIP degradation

CIP, a type of antibiotic belonging to the quinolone class, is extensively used in medical treatments, animal husbandry, agriculture, and aquaculture. It is useful for protecting against various diseases, including infection of bones and joints, endocarditis, gastroenteritis, urinary tract infections, respiratory tract infections, *etc.* Due to its versatility regarding various diseases, it is consumed globally at a large scale. After usage or production, a considerable quantity of residues come into the environment, and they easily infiltrate into water bodies, leading to the emergence of antibiotic-resistant strains and causing significant pollution to aquatic ecosystems. Moreover, CIP produces biotoxins that harm the human central nervous system, liver, kidney, and circulatory system. Photocatalysis has been widely recognized as an effective method for remediating CIP in water, offering advantages such as low energy consumption, cost efficiency, and operational convenience[110]. However, most catalysts suffer from drawbacks like rapid recombination of photoinduced electron-hole pairs and a slow reaction rate, limiting their practical application in water purification[111]. Consequently, the development of efficient materials with exceptional performance in treating CIP in the environment remains a challenging task.

As a result, it demonstrates exceptional photocatalytic degradation capabilities and has found extensive applications in the treatment of wastewater containing CIP pollutants[112]. In recent times, there have been several noteworthy studies that have explored the use of POMs as photocatalysts in the degradation of CIP.

Brahmi *et al.* conducted a study to assess the efficacy of newly developed POM/polymer composites for removing CIP from water[88]. The experiments conducted during the study highlighted the crucial role of the phosphomolybdic acid-based composite in completely degrading CIP. Through simple photolysis under UV-visible light irradiation, CIP could be effectively eliminated from water. However, the study did not experimentally demonstrate the recyclability of the developed immobilized photocatalyst. Nonetheless, regeneration capability was tested on the photodegradation of a selected dye, and it was observed that the composite's effectiveness decreased starting from the 5th cycle. This reduction may be attributed to the complete reduction of the POM metallic center, necessitating a slow reoxidation with air or rapid

reoxidation with strong oxidants such as H_2O_2.

He *et al.* conducted a synthesis of nitrogen-deficient g-C_3N_4 loaded with POMs porous photocatalysts featuring P-N heterojunctions[108]. This synthesis involved the formation of chemical bonds between nitrogen-deficient C^+ in g-C_3N_x and bridging oxygen in POMs, including phosphomolybdic acid (PMA), phosphotungstic acid (PTA), and silicotungstic acid (STA). Adsorption and photocatalysis experiments were conducted to assess the efficacy of g-C_3N_x/POM nanosheets in the removal of CIP [Figure 5], employing synergistic effects of adsorption and photocatalysis. Among the composites prepared with different mass ratios, g-C_3N_x/POMs-30 (30% wt.%) demonstrated the highest degradation ability. Under visible light, g-C_3N_x/PMA-30, g-C_3N_x/PTA-30, and g-C_3N_x/STA-30 achieved CIP degradation up to 93.1%, 97.4%, and 95.6%, respectively, within a mere 5-min duration. The incorporation of Keggin-type POMs into porous g-C_3N_4 nanosheets resulted in enhanced light absorption and improved efficiency in separating electron-hole pairs, thereby resulting in a much higher photocatalytic activity. Free radical scavenging and ESR free radical capture experiments confirmed that ·OH and $\cdot O_2^-$ were effective radicals for the degradation of CIP.

Application of POMs and their composites in SMX degradation

Like TC and CIP, SMX is another widely used drug. It is one of the most prominent members of the sulfonamide group of drugs often used for the treatment of bacterial infections, urinary tract infections, bronchitis, *etc.*[113]. It works well against both gram-positive and gram-negative bacteria such as *Streptococcus pneumoniae*, *Escherichia coli*, *Klebsiella species*, *etc.* It is widely used for human and veterinary medication purposes and is classified as a high-priority drug. It is generally consumed orally with water. Some studies have been reported in recent times regarding the application of POM-based composite catalysts for degrading SMX in water medium. Zhang *et al.* prepared a novel ternary composite catalyst C-dots/$SrTiO_3$/$NH_4V_4O_{10}$ and applied it for the oxidative abatement of drug compounds such as SMX, CIP, and aureomycin hydrochloride[114]. Under optimized conditions, an excellent degradation efficiency of 94.7% has been achieved for SMX. Experiments were carried out with an initial concentration of the drug compound as 15 mg/L under the exposure of simulated sunlight. The reaction proceeded via the Z-scheme mechanism and showed good reusability up to four cycles. A type II heterojunction mechanism was also proposed. However, it was not consistent with the ESR result. The schematic for both the mechanisms (type II and Z-scheme) is shown in Figure 6. Detailed investigations revealed that hydroxyl radicals played a crucial role in photodegradation of SMX.

Yang *et al.* tested the photocatalytic activity of Fe-polyoxometalate decorated Bi_2MoO_6 nanosheets towards the degradation of TC[93]. It showed promising performance in TC removal. Moreover, as reported by the authors, the intermediate products were also not found harmful, and the degradation efficiency was retained throughout the wide range of pH 3-11. Apart from TC, the newly synthesized catalyst was also tested against SMX, where remarkable performance was achieved. In another work, Zhang *et al.* explored the photocatalytic efficiency of the composite catalyst N-$SrTiO_3$/$NH_4V_4O_{10}$ towards oxidative degradation of SMX in aqueous solution[115]. $NH_4V_4O_{10}$, $SrTiO_3$, and N-doped $SrTiO_3$ were abbreviated as NVO, STO, and NSTO. From the Scanning Electron Microscopic (SEM) analysis, it was observed that NVO possessed a layer-like structure, whereas STO revealed a nanosphere-like morphology. It was quite interesting to observe that due to N doping, the diameter of N-STO microspheres was reduced in comparison to the pristine STO. Moreover, the SEM and Transmission Electron Microscopic (TEM) image of the developed catalyst proved that a uniform loading of N-STO took place on the surface of NVO and heterojunction was successfully formed. Experimentally, it was found that 30 wt% loading of N-$SrTiO_3$ (NSN-30) was the most efficient catalyst. Primarily, the traditional type II heterojunction principle was proposed for the degradation mechanism. However, due to a contradiction with the EPR result, the S-scheme mechanism was found to be more suitable.

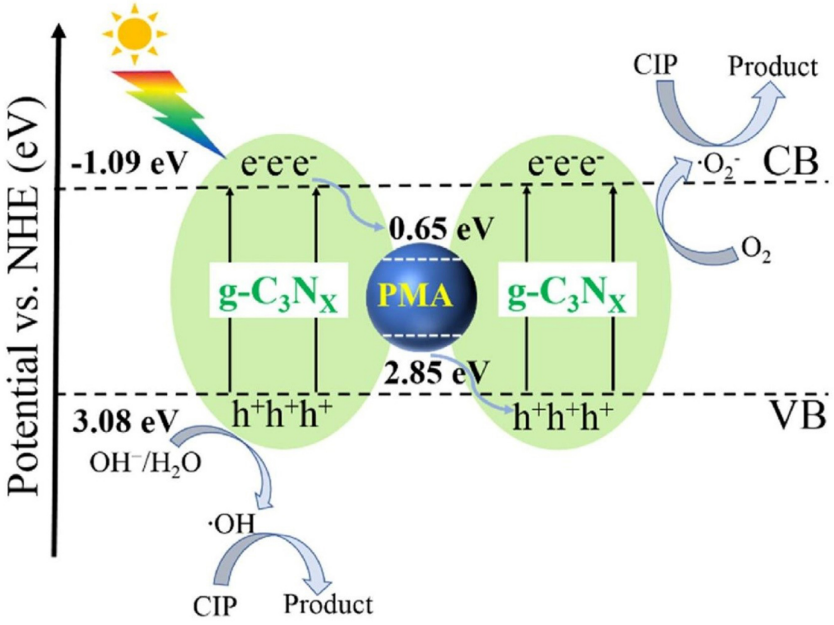

Figure 5. The proposed mechanism for the photodegradation of CIP on the surface of g-C_3N_x/POMs nanocomposites[108]. CB: Conduction band; CIP: ciprofloxacin; PMA: phosphomolybdic acid; VB: valence band.

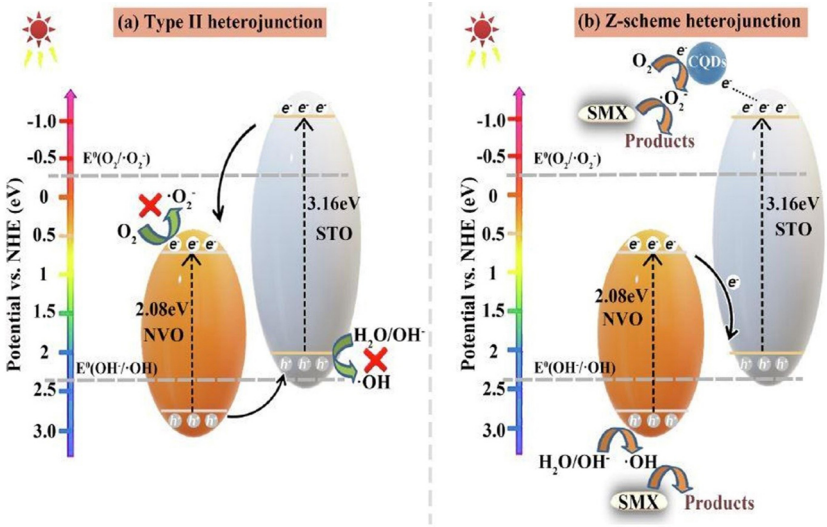

Figure 6. Z-scheme charge transfer mechanism at 5CSN-8 interface[114]. NVO: $NH_4V_4O_{10}$; SMX: sulfamethoxazole; STO: $SrTiO_3$.

Liu *et al.* utilized an $Ag_3PO_4/Bi_4Ti_3O_{12}$ heterojunction catalyst for the degradation of SMX drugs[116]. The composite catalyst exhibited higher removal efficiency in comparison to pure Ag_3PO_4 and pure $Bi_4Ti_3O_{12}$. The photocatalytic reaction was performed under the exposure of 300-W Xenon lamp irradiation using a filter ($\lambda > 400$ nm) with an initial concentration of SMX as 5 mg/L. Around 80% oxidation took place within 40 min with a reaction rate constant of 0.035 min^{-1}. It was deduced that the photocatalytic degradation occurred via direct Z scheme mechanism, and h^+ was the main species responsible for the SMX removal. POM-based catalysts explored for degrading CIP and SMX have been compiled in Table 2.

Table 2. Summary of SMX and CIP degradation studies by various POMs/POM-composites

POM composites	Reaction condition	Removal efficiency	Ref.
$H_3PMo_{12}O_{40}$/polymer and $W_{10}O_{32}$ $(TH)_4$/polymer composites	Initial concentration of CIP = 15 mg/L, pH = 6.3, in photometer cell	Complete degradation in 90 min	[88]
g-C_3N_x/POM nanosheets	At a catalyst dose of 0.4 g/L, initial concentration of CIP = 20 mg/L, under visible light irradiation (300 W Xenon lamp)	97.3% removal in 5 min	[108]
Ternary C-dots/$SrTiO_3$/$NH_4V_4O_{10}$ Z-scheme heterostructure	With an initial concentration of SMX = 15 mg/L, under exposure to solar light	Degradation of 94.7%	[114]
N-$SrTiO_3$/$NH_4V_4O_{10}$ S scheme	At a catalyst dose of 1.5 g/L, initial concentration of SMX = 10 mg/L, under visible light irradiation for 120 min	Degradation of 90.5%	[115]
Direct Z scheme Ag_3PO_4/$Bi_4Ti_3O_{12}$	Under irradiation of visible light of 300 W Xenon lamp with an initial concentration of SMX = 5 mg/L	Nearly 80% degradation in 40 min reaction time	[116]

CIP: Ciprofloxacin; POM: polyoxometalate; SMX: sulfamethoxazole.

Application of POMs and their composites in degradation of other antibiotics

Apart from the commonly used pharmaceuticals mentioned in the previous sections, some other antibiotics reported in the literature were successfully degraded by means of the application of POM-based catalysts. Wang *et al.* prepared a novel POM-based complex $[Cu_2(1,10\text{-phenanthroline-}5,6\text{-dione})_3(PMo_{12}O_{40})]_2{\cdot}3H_2O$ (shown in Figure 7) and deployed it for the degradation of metronidazole[117]. The addition of NaCl slightly improved the degradation efficiency. In the absence of NaCl, nearly 71% degradation was achieved after being illuminated under UV light for 150 min. On the other hand, in the presence of NaCl, 81% removal efficiency was obtained. In addition, solution pH also played a significant role in metronidazole oxidation. At an acidic pH (~3), nearly 67% degradation occurred, while at a higher pH (~9), only 34% oxidation took place. In another study, Wang *et al.* used two POM-based composite materials $[Cu(Dione)_2H_2O]_2Cl{\cdot}(PMo_{12}O_{40})$ and $[Cu(En)_2H_2O]_4{\cdot}[Cu(En)_2(PW_{12}O_{40})]_2{\cdot}(PW_{12}O_{40})_2{\cdot}2H_2O$ for the photocatalytic degradation of antibiotics such as cefalexin and ceftiofur[118]. In the presence of the second catalyst, a promising removal of 90.61% was obtained in the case of ceftiofur. Moreover, it showed excellent reusability up to five cycles without any appreciable loss in catalytic activity.

Brahmi *et al.* prepared a novel POM/polymer composite for the eradication of four model PCs such as CIP, OTC, Ibuprofen (Ibu), and erythromycin through a photocatalytic mechanism[88]. For different drugs, different results were obtained. It was found that for degrading CIP and OTC, removal was feasible by simple photolysis and UV light exposure, even in the absence of catalysts. However, for Ibu, the presence of the POM/polymer composite enhanced degradation efficiency drastically. However, in the case of erythromycin, the removal efficiency was diminished in the presence of the POM/polymer catalyst.

Decatungstate ($W_{10}O_{32}^{4-}$) anion has been reported as an efficient POM for the degradation of organic pollutants. Cheng *et al.* utilized sodium decatungstate ($Na_4W_{10}O_{32}$) as a sacrificial agent for the degradation of the pharmaceuticals sulfasalazine and sulfapyridine[87]. In the presence of H_2O_2, $W_{10}O_{32}^{4-}$ is reduced to $W_{10}O_{32}^{5-}$, leading to the generation of hydroxyl radical. Li *et al.* reported the synthesis and application of novel POM-metal organic framework(MOF)-based composite PW_{12}@MFM-300(In) towards photocatalytic degradation of sulfamethazine in water medium[119]. Around 98% degradation took place within two hours under visible light irradiation. Further experimental analysis revealed that the indium-oxygen cluster and organic bridging ligands of the MOF host acted as the quantum dots and antennas. On being exposed to visible light, photo-generated electrons are transferred from the valence band of MFM-300(In) to the conduction band of PW_{12}, causing photocatalytic activity. Further, these photo-generated electrons are captured by H_2O_2 to produce strong hydroxyl radicals to facilitate the reaction.

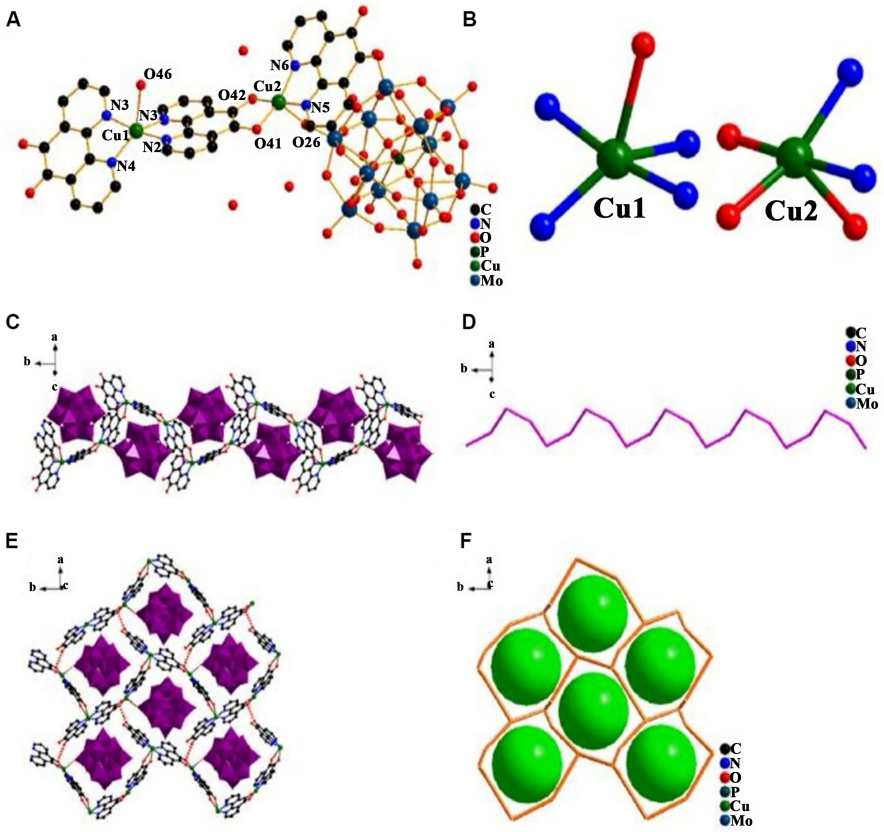

Figure 7. (A) The asymmetric unit of complex 1; (B) Coordination mode of Cu1 and Cu2; (C) One-dimensional structure; (D) Zigzag structure; (E) Two-dimensional structure constructed by hydrogen bonding; (F) $(PMo_{12}O_{40})^{3-}$ nucleus and polygonal frame[117].

Selvakumar *et al.* used Sm_2MoO_6/ZnO/rGO composite for the photocatalytic degradation of the Ibu drug molecule[120]. The composite catalyst was prepared by simple hydrothermal method, and from the experimental investigation (UV-DRS study), it was revealed that it possessed the lowest bandgap (i.e., 3.12 eV) amongst Sm_2MoO_6, ZnO, and Sm_2MoO_6/ZnO. In the presence of visible light, within 90 min, almost complete (96.73%) degradation of Ibu took place.

From the self-assembly of β-cyclodextrin and POM, a composite material was produced and deployed for the catalytic degradation of various dyes as well as antibiotic compounds such as nitrofurazone, TC, and berberine in the presence of H_2O_2[22]. The schematic of the composite formation and organic compound degradation is shown in Figure 8.

Briefly, the catalytic potential was tested against an initial concentration of 0.033 mM of nitrofurazone. In the composite catalyst, the content of POM was kept as 0.055 mM and 0.03 mM polycationic per-6- deoxy-6-ethylenediamine-β-cyclodextrin (EDA-CD). After 15 min from the start of the reaction, 50 μL of H_2O_2 was added, and the degradation percentage was monitored from time to time. Complete catalytic degradation of nitrofurazone occurred within 19 min under the exposure of a 50-W mercury lamp.

Yang *et al.* prepared novel POM@MOF hybrid-derived hierarchical hollow Mo/Co bimetal oxides and deployed them for levofloxacin degradation purposes via peroxymonosulfate activation[121]. The as-prepared catalyst showed promising performance and excellent reusability. Moreover, it has been found workable

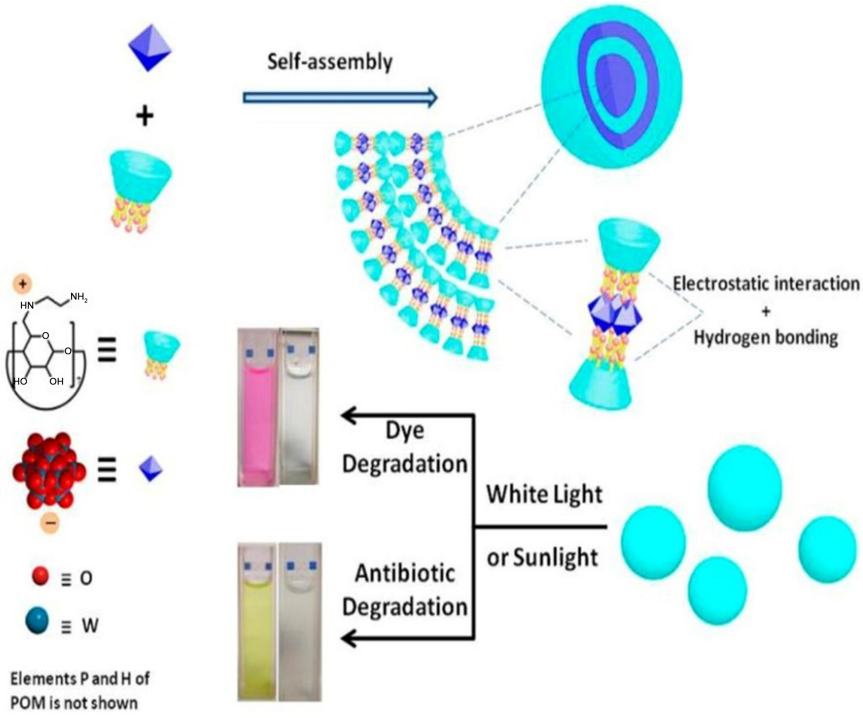

Figure 8. Possible self-assembly models of EDA-CD and POM, and hybrid nanoparticles, chemical formula, and corresponding cartoon representations of EDA-CD and POM[22]. EDA-CD: Ethylenediamine-β-cyclodextrin; POM: polyoxometalate.

throughout a wide pH range of 3-11, making it suitable for diversified types of wastewater. A tabular representation [Table 3] is provided related to the catalytic degradation of other drugs by application of POM-based composites.

Bastami and Ahmadpour[122] modified the γ-Fe_2O_3/$SrCO_3$ with $PW_{12}O_{40}^{3-}$ anions to prepare a novel hybrid catalyst for degrading Ibu drug. Under solar light irradiation, in the presence of H_2O_2, almost complete degradation occurred in 2 h reaction time.

STABILITY OF POMS IN SOLUTION

A catalyst should be chemically stable enough to be suitable for real field applications. It is already mentioned earlier that POMs are formed due to the lowering of pH of the neutral solutions of salts of transition metals, e.g., Mo, W, V, Nb, *etc.* In many studies, the stability of the POM-based catalysts has been reported as one of the crucial parameters affecting the overall removal efficiency of the target pollutant. Cheng *et al.* studied the effect of the solution pH on the stability of the composite photocatalyst as well as the removal efficiency of sulfasalazine and sulfapyridine[87]. The degradation rate constant of both the PCs was enhanced at a lower pH of 3 and decreased at a higher pH of 6. Moreover, as per other reported studies, the stability of decatungstate gets diminished at a higher pH. However, some other studies reported a reverse phenomenon regarding the degradation and stability of the catalyst with respect to the solution pH. Xing *et al.* reported that the optimum pH for POM-anchored zinc oxide nanocomposite to degrade TC is around 7[103]. Liu *et al.* found that a high pH condition is favorable for the degradation[98]. In the study of degradation of five PCs, TC, ofloxacin (OFL), norfloxacin (NOR), CIP, SMX by application of Fe-POM nanodots decorated Bi_2MoO_6 nanosheets, it was quite interesting to observe that the catalytic efficiency as well as the stability of the nanocomposite was retained in a wide pH range (3-11)[93]. The removal efficiency of TC throughout a wide pH range is shown in Figure 9.

Table 3. Degradation efficiency of POM-based catalysts towards other drug compounds

POM composite	Target drug compound	Maximum degradation efficiency	Ref.
Self-assembled structure of β-cyclodextrin and POM	Nitrofurazone, TC and berberine	Complete degradation of nitrofurazone. TC, and berberine in 19, 25 and 30 min	[22]
Sodium decatungstate	Sulfasalazine and sulfapyridine	-	[87]
POM-supported on biochar	NOR, SMX, TC	99.6%, 99%, and 100% removal for NOR, SMX, and TC, respectively	[94]
$[Cu(Dione)_2H_2O]_2Cl·(PMo_{12}O_{40})[Cu(En)_2H_2O]_4·[Cu(En)_2(PW_{12}O_{40})]_2·(PW_{12}O_{40})_2·2H_2O$	Cephalexin and ceftiofur	The degradation rate of ceftiofur reached up to 90.61%	[117]
$[Cu_2(1,10\text{-phenanthroline-}5,6\text{-dione})_3(PMo_{12}O_{40})]_2·3H_2O$	Metronidazole	Degradation rate of metronidazole reached up to 80.2%	[118]
Phosphotungstic acid incorporated into a metal-organic framework [PW12@MFM-300(In)]	Sulfamethazine	98% degradation in 2 h	[119]
Sm_2MoO_6/ZnO/rGO	Ibu	96.73% photodegradation under visible light illumination within 90 min	[120]
POM@MOF hybrid derived hierarchical hollow Mo/Co bimetal oxides nanocages	Levofloxacin	With an initial concentration of levofloxacin as 10 mg/L, at pH 7, at a catalyst dose of 0.1 g/L, in the presence of 1 mM PMS, around 90% degradation	[121]

MOF: Metal organic framework; NOR: norfloxacin; PMS: peroxymonosulfate; POM: polyoxometalate; SMX: sulfamethoxazole; TC: tetracycline.

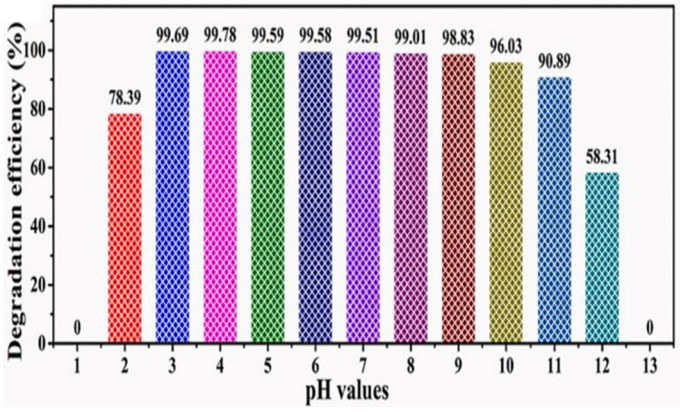

Figure 9. Degradation of TC over a wide range of pH[93]. TC: Tetracycline.

Aureliano, in his recent review article, highlighted the importance of the stability of the POM-based composites regarding environmental application[123]. It is mentioned that decavandate (V_{10}) is often explored for various environmental applications. Many studies reported that in the presence of proteins (actin, Ca^{2+}-ATPase), the stability of V_{10} is improved significantly.

CURRENT KNOWLEDGE GAP AND FUTURE PERSPECTIVE

Undoubtedly, POMs are excellent new-age materials that can be effectively utilized for catalytic degradation of PCs in water bodies. They possess several distinguishing properties that can be of immense help in view of wastewater treatment. However, there are several issues and a huge knowledge gap that must be bridged in order to efficiently use these catalysts for industrial purposes.

Recepoglu *et al.*, in their recent review, highlighted the fact that relatively less research work has been carried out on forming magnetic composites with the POMs[124]. Formation of magnetic composite often helps in easy recovery of the catalyst material and helps in recyclability. Bastami and Ahmadpour[122] prepared a novel POM magnetic nanohybrid catalyst for the degradation of Ibu under solar light irradiation.

MOFs have been proven to be an excellent modifier for POMs. However, to date, only a handful of MOFs have been explored for this purpose, as highlighted by D'Cruz *et al.* in their recent review article[125]. Other MOFs need to be explored in order to know their suitability for the purpose.

For industrial applications, one of the most important criteria is the suitability of the catalyst in the presence of other coexisting ions. Hence, more studies are recommended to have a thorough idea regarding the influence of other ions on POM-based catalysts for PC degradation purposes.

Lan *et al.*, in their recent critical review, described several drawbacks that need to be overcome in the near future for making POM-based composites as novel materials for real wastewater treatment[126]. Most of the POM-based catalysts are based on some classic clusters such as Keggin, Dawson, and Anderson. So, it is clear that more exploration is still required at the atomic level. Additionally, a detailed study of the mechanism is recommended. One of the most critical drawbacks of the POM-based composites is their leaching into the medium during the course of the reaction. It is mentioned that most of these composites are prepared through hydrothermal, impregnation, self-assembly, and sol-gel methods, and they remain attached to the support material by simple non-covalent interaction. Hence, there is a huge possibility that these materials will get detached from the support materials after some cycles of catalytic reaction. Recepoglu *et al.* mentioned some major drawbacks apart from describing the universal application of POM-based composites for wastewater treatment[124]. It is also mentioned that more effort is required to monitor the design of the POM composite in order to achieve minimal leaching during the course of the reaction. Moreover, as it is an emerging field in the area of wastewater engineering, more studies on real wastewater effluents, along with modeling, are required. Emphasis is needed on the application of POM composites for the large-scale wastewater treatment plant as well as for commercialization purposes.

CONCLUSIONS

POM-based catalysts have proved to be an excellent new-age material for pharmaceutical wastewater remediation. These novel catalysts have been found promising in degrading commonly encountered antibiotics such as TC, SMX, CIP, Ibu, *etc.* Reactive oxygen species such as hydroxyl radical and singlet oxygen often play a vital role in the mineralization of PCs. In addition to the single compound, these catalysts have also shown good performance in degrading wastewater effluents containing multiple drugs. Hence, these catalysts are well-suitable for treating real wastewater. However, most of the catalysts reported are only applicable to lab-scale studies. So, further research work is recommended for scaling up. Only a handful of POMs have been explored till now. There is also a huge prospect of developing new catalysts by forming composites with other new-age materials.

DECLARATIONS

Authors' contributions

Writing of the original draft, literature review: Pal D
Writing, review: Biswas S, Nayak AK
Writing, review, supervision: Pal A

Availability of data and materials
Not applicable.

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Conflicts of interest
All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

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