RESEARCH PROGRESS ON POLYOXOMETALATES AS PHOTOCATLYTIC MATERIAL

A MSc Dissertation report by;

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DECLARATION

I declare that the literature review titled "RESEARCH PROGRESS ON POLYOXOMETALATES AS PHOTOCATLYTIC MATERIAL" has been carried out by me in the Chemistry Department, School of Chemical Sciences, Goa University. The Information derived from the literature has been duly acknowledged in the text and a list of references is provided**.**

AKNOWLEDGMENT

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There is no good work done which comes without efforts; but those efforts cannot be obtained without proper guidance. So, in these few humble lines I take this opportunity to express my profound gratitude to the people who have made invaluable contribution during the course of completion of the literature review in time.

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INTRODUCTION

We benefit from the speed of modern life, but our lifestyle is accompanied by increasingly serious environmental problem such as organic pollutants, wastewater, dyes (especially azo dyes), medical wastes etc. So as to remove these types of pollutants uses green photocatalysts to remove out these pollutants or decrease the environmental pollution.[1–3] In recent decades, POMs have received a lot of attention because of their good performance under homogeneous or heterogeneous photocatalytic processes.[4,5] Polyoxometalates (POMs) are metal–oxygen anion nano-clusters which consist of abundant oxygen atoms and early transition metals (including Mo, W, V, Nb, and Ta) in the highest oxidation state and are usually prepared through the condensation procedure of metal salts in solution (generally in water) at an appropriate pH value and temperature.[6]

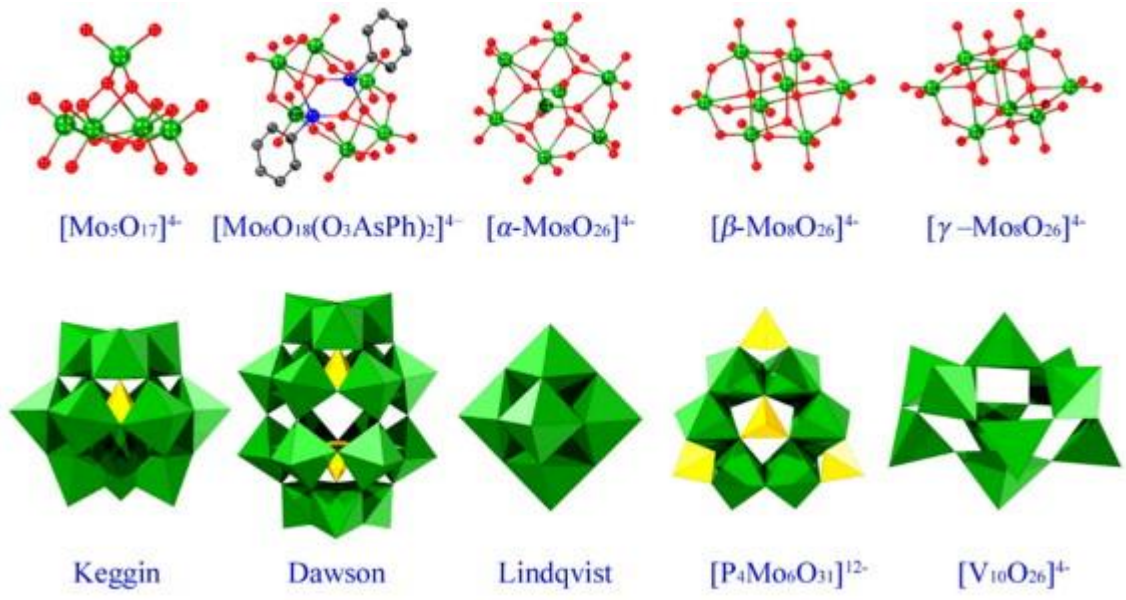


Fig 1; Examples of polyoxometalates.

A variety of photochemical conversion processes are driven by homogeneous and heterogeneous photocatalysts, where an electron transfer reaction is initiated by absorbing sufficient energy near the ultraviolet or visible light spectrum.[5,7] POMs are a vast class of green, cheap and stable early transition metal–oxygen clusters which exhibit semiconductor-like photochemical behaviours due

to analogous electronic characteristics (band gap transition for semiconductors and HOMO–LUMO transition for POMs).[8] POMs function as green catalysts in a variety of areas and can also be used as multifunctional catalysts when combined with other catalysts. [8]

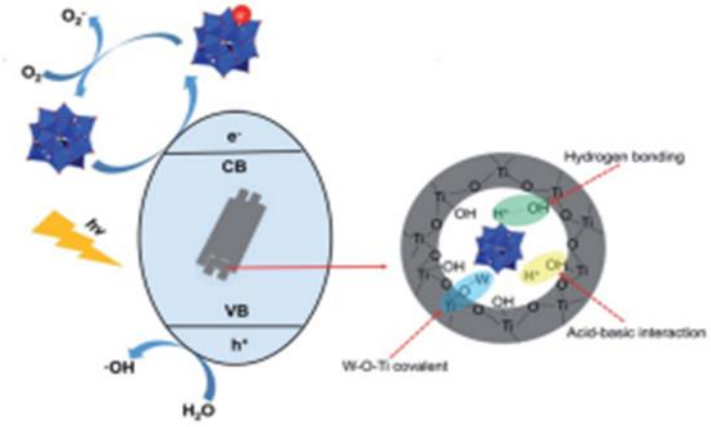


Fig 2; Structure and photocatalytic mechanism of the POM / TiO2 composite material[9]

The specific surface areas of the supported POMs are largely increased compared with the parent POMs (BET specific surface areas of POMs are lower than 10 m2/g). This larger surface area may result in an increase in the catalytic activity of POMs by providing large contact areas between the catalyst and substrate for the surface-mediated electron-transfer reactions. Fixing POMs on porous metal–organic frameworks (POMOFs) structures can increase the surface area while maintaining their excellent catalytic performance.[10] In 1985, the Hill's group studied the photocatalytic chemistry of POMs, and a reasonable model was proposed to explain the relationship between the light absorption wavelength of POM-organic matrix system and the photochemical reaction system.[9] The photochemical properties of most POMs are very similar to those of semiconductor photocatalysts, and POMs are analogues of semiconductor metal oxides. That is, both classes of materials are composed by d^0 transition metal and oxide ions and exhibit similar electronic properties including well-defined HOMO–LUMO gaps (semiconductor "bandgaps"). By irradiating the surface of the photocatalysts with light energy higher than or equal to their band gap energy, they inhibit the recombination of electrons and holes. Due to the strong photooxidative ability of holes and the strong photo reductive ability of electrons, these photogenerated electrons and holes are capable of initiating a chemical reaction.[8]

Further feasible applications can be made possible through the functionalization of inorganic POMs, as it can regulate their physical and chemical properties.[9,11] To functionalize POMs, there are generally three main approaches:(1) The solubility of POMs can be adjusted by exchanging the counterions (POMs usually possess negative charges) with organic cations;(2) Inorganic ligands such as POMs have abundant surface oxygen and can be used to build high-dimensional coordinated complexes with metal ions; (3) POMs can be covalently modified using organic ligands, which is conducive to the design of inorganic-organic hybrid materials based on POMs.[9]

There are numerous advantages of using POMs as photocatalysts: [9,11]

- Transition metals (such as Mo, W, V, Nb, and Ta) are abundant in POMs, and a significant number of potential active sites are visible on the surface.
- To increase the photo-catalytic performance of POMs, the band gap may be altered by altering the heteroatoms (such as P and Si) or shifting the valence states of metal atoms in their structures.
- Organic ligands may be used to functionalize POMs, and they can also be loaded on matrix materials (such as TiO2, carbon nanomaterials, and other support materials) to achieve a synergistic impact between diverse components.
- Single crystal X-ray diffraction can definitively determine the molecular structure of POMs, which is useful for exploring the structure–function relationship at atomic resolution.

As a result, there is a growing body of knowledge on POM-based photocatalysts for photodegradation of organic pollutants, including structural design, photocatalytic characterization, degradation medical waste and kinetics of transformation.[9,11–13] Recent research findings suggest that creating enhanced POM-based photocatalysts, from preparation to applications, has a promising future. More inventive discoveries of POM-based materials are

predicted in the future, especially in green energy conversion and environmental research, if ongoing efforts continues.

Photocatalytic mechanism of POMs

POMs have an electrical structure similar to that of a semiconductor, with an electron-occupied valence band (VB) and an unoccupied conduction band (CB).[14] In general, as shown in Fig. 2, POMs have a semiconductor-like electrical structure, with an electron-occupied valence band (VB) and an unoccupied conduction band (UCB) (CB). In the presence of water, the positive

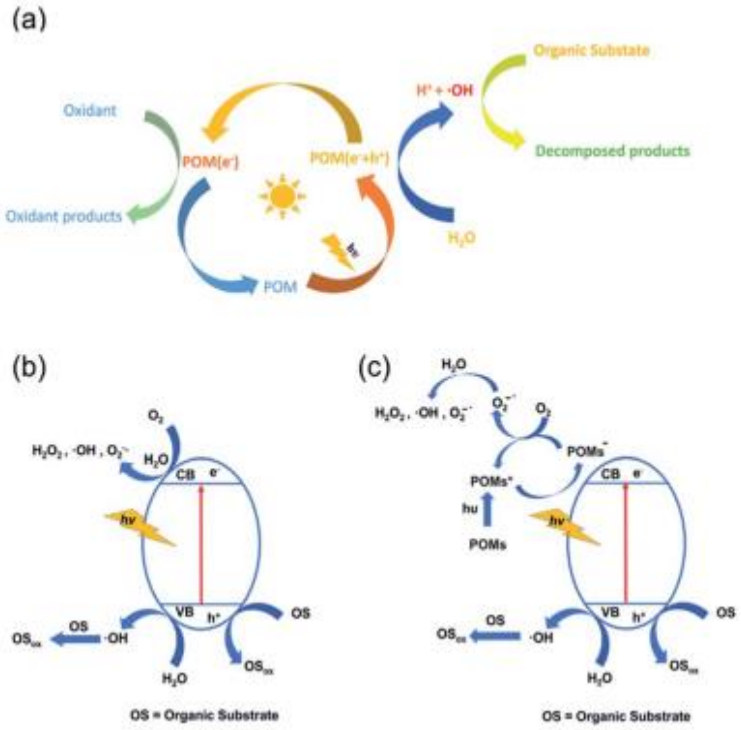


Fig. 3 ;(a) Diagrammatic scheme of the photocatalytic mechanism of POM-based catalysts; (b) the mechanism of pure POM photocatalysts; (c) the photocatalytic mechanism of POM/support composites.[9]

water, the positive holes will form hydroxyl radicals (.OH) from organic substrates. Hydroxyl radicals have been postulated as active species for the oxidation and degradation of organic substrates because of their high oxidising characteristics. (Fig. 3b). When POMs are put on photo catalytically active semiconductors like TiO2, their photo catalytic activity can be further improved.[5,15] POMs normally operate as a scavenger in this scenario, collecting photo-generated

electrons from the semiconductor and reducing the POMs species. This action slows the recombination of h+ and e couples and increases the efficiency of hydroxyl radical generation by h+ from the semiconductor. Meanwhile, the POM species donates an electron to the dissolved oxygen in the solution, producing oxygen radicals O2c, which subsequently react with water to produce(.OH) and/or H2O2, further oxidising the organic substrates. (Fig. 3c). [6] Keggin-type POMs are frequently used in photocatalytic degradation of organic contaminants because to their acceptable band gap, high stability, and ease of fabrication. After regulating the band gap via reasonable adjustment and loading, other types of POMs have possible uses as well.[6,8]

Literature review

Table 1; Polyoxometalates as photocatalytic material

Sr no	Compounds	Method of Synthesis	Applications	Year	Ref No.
1	$[Mn^{II}Mn^{III}SiW_{10}O_{37}(OH)(H_2O)]^{6-}$(Mn2-POM)	$K_{10}[Mn_4(H_2O)2(PW_9O_{34})2]\cdot15H_2O$ and K at 85 °C	Water splitting	2022	16
2	$[Mn^{II}_3Mn^{III}(H_2O)_2(PW_9O_{34})_2]^{9-}$ (Mn4-POM)	$K_{10}[Mn_4(H_2O)_2(PW_9O_{34})_2]\cdot41H_2O$ and$K_2S_2O_8$at 85◦C	Water splitting	2022	16
3	$[Mn^{II}_4Mn^{III}_2Ge_3W_{24}O_{94}(H_2O)_2]^{18-}$ (Mn_6-POM)	Na_2WO_4, GeO_2, HCl, Mn $(CH_3COO)_2\cdot4H_2O$ and imidazole at 90◦C	Water splitting	2022	16
4	$[Mn^{III}_2Mn^{II}_4(\mu_3\text{-}O)_2(H_2O)_4(B\text{-}\beta\text{-}SiW_8O_{31})$ (B-β-SiW_9O_{34}) (γ-$SiW_{10}O_{36}$)]$^{18-}$(Mn_6-POM-4)	$K_8[\gamma\text{-}SiW_{10}O_{36}]\cdot12H_2O$, $MnCl_2$ and K_2CO_3 at 40 °C.	Water splitting	2022	16
5	$[Mn^{II}_{19}(OH)_{12}(SiW_{10}O_{37})_6]^{34-}$($Mn_{19}$-POM)	Na_2wo_4NaOAc .3.H_20 HCl and dimethyl amine hydrochloride at 100 °C.	Water splitting	2022	16
6	$[\{Mn^{III}_3Mn^{IV}_4O_4(OH)_2(OH_2)\}_2(W_6O_{22})(H_2W_8O_{32})_2(H_4W_{13}O_{46})_2]^{26-}$($Mn_{14}$-POM)	$MnCl_2\cdot4H_2O$, Na_{10}[A-α-SiW_9O_{34}], NaOH, Na_3PO_4 and HCl at 70	Water splitting	2022	16
7	[Cu (Dione)$_2H_2O]_2Cl\cdot(PMo_{12}O_{40})$	hydrothermal method	photodegradation of cephalexin and ceftiofur	2022	17
8	$[Cu(En)_2H_2O]^{4\cdot}$ $[Cu(En)_2(PW_{12}O_{40})]_2\cdot(PW_{12}O_{40})_2\cdot2H_2O$	hydrothermal method	photodegradation of cephalexin and ceftiofur	2022	17

9	$[Zn_4(PO_4)(C_7H_8N_4)_6][BW_{12}O_{40}].2H_2O$	POM-based organometallo phosphate frameworks	Reduction CO_2 to chemical	2022	18
10	$[Co_4(PO_4)(C_7H_8N_4)_6][BW_{12}O_{40}]1.5H_2O$	POM-based organometallo phosphate frameworks	Reduction CO_2 to chemical	2022	18
11	$H_3PW_{12}O_{40}–TiO_2$	hydrothermal method	Degradation of dyes	2012	8
12	$H_3PW_{12}O_{40}/TiO_2$	sol–gel following hydrothermal treatment	-	2012	8
13	$[Cu_2(1,10\text{-phenanthroline-}5,6\text{-dione})_3(PMo12O40)]_2 \cdot 3H_2O$	solvothermal method	degradation of metronidazole	2022	19
14	$Ag_3PW_{12}O_{40}$/ ZnO	ZnO solution dispersed under ultrasonication for 10 min. To this $Ag_3PW_{12}O_{40}$ was added under stirring for 24 h. and the precipitate was collected	82.1% Rh B in 60 min.	2022	20
15	$[Na_3PMo_{12}V_3O_{43}] \cdot 4H_2O$	Hydrothermal method	Degradation ethylene blue, Rhodamine B and methyl orange dyes	2022	21
16	$[P^{5+}W_{11}O_{39}]^{10-}$	sol–gel and template technique	degradation of azo dyes	2012	8
17	$[si^{4+}W_{11}O_{39}]^{11-}$	sol–gel and template technique	degradation of azo dyes	2012	8
18	$[Ge^{4+}W_{11}O_{39}]^{11-}$	sol–gel and template technique	degradation of azo dyes	2012	8
19	POM $PW_{11}O_{39}Fe$ (III) $(H_2O)_4$	Hydrothermal method	degradation aqueous azo dye 7 detection of NH^{4+} NO^{3+}, and SO_4^{2-}	2014	22
20	POM $PW_{11}O_{39}Fe$ (III) $(H_2O)_4$	Hydrothermal method	Rhodamine B and nitrobenzene	2021	9
21	$K_3PW_{12}O_{40}.nH_2O$	Hydrothermal method	Rhodamine B	2021	9

Discussion

Polyoxometalates are used as photo catalytical material Recently, Wu Y, Pei J, Yu X, Bi L. Study on Catalytic Water Oxidation Properties of Polynuclear Manganese Containing

Polyoxometalates.[16] This work, by selecting from the literature, six polynuclear manganese (Mn) containing polyoxometalates were prepared, i.e (Mn-POMs) with different Mn-O clusters and oxidation states of (**1**)Mn, $[Mn^{II}Mn^{III}SiW_{10}O_{37}(OH)(H_2O)]^{6-}$(Mn2-POM), (**2**)$[Mn^{II}_3Mn^{III}(H_2O)_2(PW_9O_{34})_2]^{9-}$(Mn4-POM), **(3**)$[Mn^{II}_4Mn^{III}_2Ge_3W_{24}O_{94}(H_2O)_2]^{18-}$(Mn6-POM-1), (**4**)$[Mn^{III}_2Mn^{II}_4(\mu3\text{-}O)2(H_2O)4(B\text{-}\beta\text{-}SiW_8O_{31})(B\text{-}\beta\text{-}SiW_9O_{34})(\gamma\text{-}SiW_{10}O_{36})]^{18-}$(Mn6-POM-4), (**5**)$[\{Mn^{III}_3Mn^{IV}_4O_4(OH)_2(OH_2)\}2(W_6O_{22})(H_2W_8O_{32})_2(H_4W_{13}O_{46})2]^{26-}$(Mn14-POM),

Abbreviation	Chemical Formula	N (Mn^{II})	N (Mn^{III})	N (Mn^{IV})	Total N (Mn)
Mn_2-POM	$[Mn^{II}Mn^{III}SiW_{10}O_{37}(OH)(H_2O)]^6$	1	1	0	2
Mn_4-POM	$[Mn^{II}_3Mn^{III}(H_2O)_2(PW_9O_{34})_2]^9$	3	1	0	4
Mn_6-POM-1	$[Mn^{II}_4Mn^{III}_2Ge_3W_{24}O_{94}(H_2O)_2]^{18}$	4	2	0	6
Mn_6-POM-4	$[Mn^{III}_2Mn^{II}_4(\mu_3\text{-}O)_2(H_2O)_4(B\text{-}\beta\text{-}SiW_8O_{31})(B\text{-}\beta\text{-}SiW_9O_{34})(\gamma\text{-}SiW_{10}O_{36})]^{18}$	4	2	0	6
Mn_{14}-POM	$[\{Mn^{III}_3Mn^{IV}_4O_4(OH)_2(OH_2)\}_2(W_6O_{22})(H_2W_8O_{32})_2(H_4W_{13}O_{46})_2]^{26}$	0	6	8	14
Mn_{19}-POM	$[Mn^{II}_{19}(OH)_{12}(SiW_{10}O_{37})_6]^{34}$	19	0	0	19

(**6**)$[Mn^{II}_{19}(OH)_{12}(SiW_{10}O_{37})6]^{34-}$(Mn19-POM) for the Splitting of water to produce oxygen and hydrogen is a green and best method to produce clean energy .16 This prepared POMs are characterized by the UV-vis spectroscopy and cyclic voltammetry and then used in catalytical water splitting of the oxidative performance of this prepared compounds under the same experimental conditions and comparative study. The results show that Mn-POMs having three-dimensional structures, which comprise variable valence Mn-O clusters corresponding to the structure of the photocatalytic active core, perform better catalytic activity. After comparing the six Mn_xPOMs, it was discovered that Mn14-POM had the best electrocatalytic performance for water oxidation.

Mn14-POM was synthesized from precursor Mn12-acetate,Na_2WO_4 , NaOAc·3H2O, HCl and dimethylamine hydrochloride at 100 °C. The compound contains a total of 14 Mn centers, which

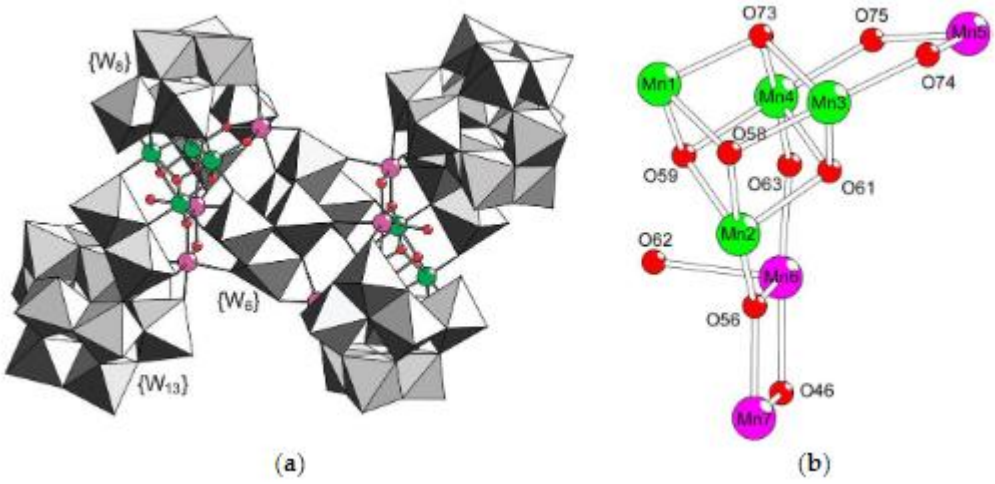


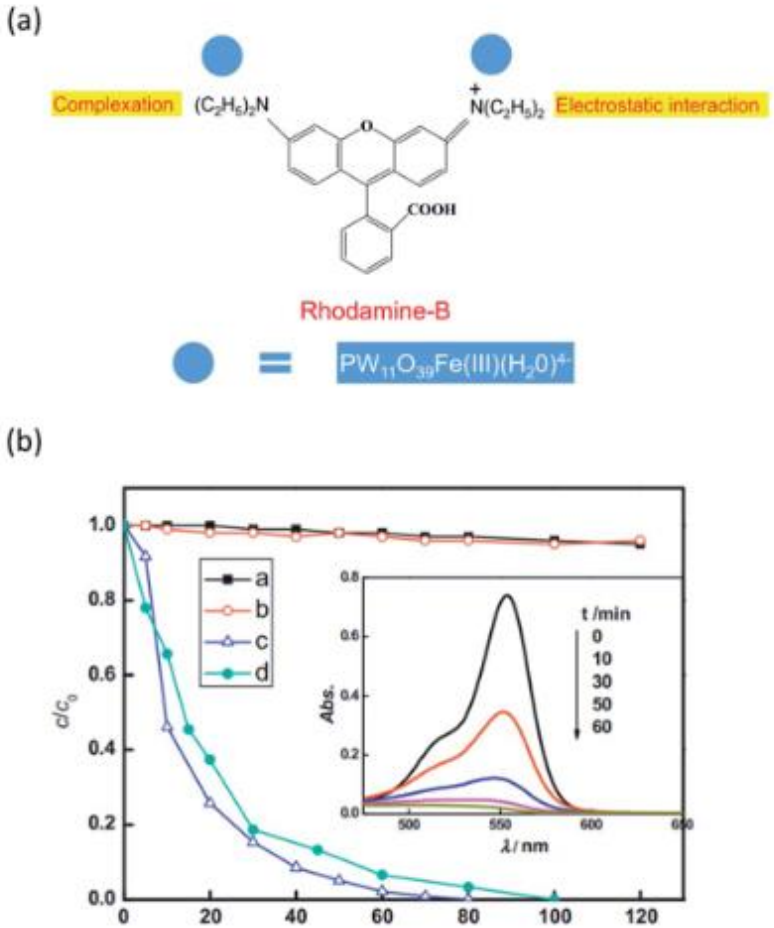
Figure 4(a) Structure of Mn14-POM. Mn (III), purple; M(IV), green; WO_6, gray octahedra; O, red.(b) Magnetic cores of Mn7[16]

are divided into a pair of Mn7 cores. Each core is embedded in the shell of diamagnetic isopolytungstate ligand and well separated from the other. The structure of Mn7 is shown in Figure 4. Each Mn7 includes a [MnIV4O4]8+ cubic unit, and three Mn (III) are connected at the periphery. The compound contains 8 tetravalent manganese and 6 trivalent manganese.[6]

In recent studies, Because of their semiconductor-like features, POMs are considered attractive candidates for photocatalytic degradation of organic contaminants. In 2021 Lan J, Wang Y, Huang B, Xiao Z, Wu P. Application of polyoxometalates in photocatalytic degradation of organic pollutants.[9] This study highlights current developments in the design and synthesis of POM-based photocatalysts, as well as their use in the degradation of organic dyes, pesticides, and other contaminants.[9] For a long time, POM-based catalysts have been used in the photodegradation of dyes since mostly the azo dyes are used in textile industries, so remove the pollutant from the environment which was present in wastewater or in the soil. Many POMs, particularly Keggin-type clusters, have demonstrated strong dye degradation photocatalytic activity.[9] The most of the POMs such as ;table 1 $K_3PW_{12}O_{40}nH_2O$, POM $PW_{11}O_{39}Fe$ (III)$(H_2O)_4$, POM $PW_{11}O_{39}Fe$

(III)$(H_2O)_4$, $[Na_3PMo_{12}V_3O_{43}] \cdot 4H2O$ are synthesized by hydrothermal method and also there are some POMs(from the above table 1) are synthesized by sol-gel method. These POMs are used in photocatalytical degradation of various dyes such asazoic (Congo Red(CR), Methyl Orange (MO), Ponceau G (PG), Orange II (alsotermedAO7), and Eriochrome Blue Black B (EB)), or anthra-quinonic (Alizarin S (AS)), or heteropolyaromatic (MethyleneBlue (MB)), or fluorescent (Neutral Red (NR), Rhodamine B(RB)), or sulfonic (Fuchsin Acid (FA)) and the intermediates and final products of degradation were detected by ion chromatography (IC) and electrospray mass spectrometry (ES-MS). Under visible-light irradiation in aqueous solutions, the mechanism of photodegradation of organic contaminants on the as-prepared catalyst was due to O2 /OH–.

For example, In 2012 Wang and coworkers studied the photocatalytic properties of Fe(III)-substituted Keggin-type POM $PW_{11}O_{39}Fe(III)(H_2O)^{4-}$ ($PW_{11}Fe$) under visible light irradiation(fig 5) .[9] In the photodegradation of Rhodamine B (RhB) and nitrobenzene, this catalyst showed significant activity (NB). It may totally decompose RhB in 80 minutes in a homogenous reaction. Fig. 5(a) Illustration of the interaction between PW11Fe and RhB; (b)photocatalytic degradation of RhB and NB under visible-light irradiation, black line:



RhB under visible-light irradiation; red line: RhB andPW_{11} Fe under dark conditions; blue line and inset graph: RhB andPW_{11}Fe under visible-light irradiation; green line: NB and PW11Fe under visible-light irradiation. [9] The iron hetero-atom performed a vital part in the catalytic process, according to the mechanism research. Charge transfer from the HOMO of PW11Fe, which is mostly made up of the p orbital of the terminal oxygen, to the iron d orbital at the site of H2O complexing with Fe(III) happened during visible light stimulation, resulting in the oxidation of H2O molecules and the generation of hydroxyl radicals. Organic dyes decompose and mineralize as a result of hydroxyl radicals, which are powerful oxidants. The Fe(III)center, on the other hand, was reduced to the unstable Fe(II), which then reduced the dissolved oxygen molecules to H_2O_2 before being restored to Fe(III). Additionally, this photocatalyst achieved excellent stability and may be reused several times without significant activity loss. This research shows that POMs with transition metal substitutes are more promising photocatalysts for dye gradation driven by visible light.[9]

Antibiotics such as penicillin and metronidazole are currently the most regularly prescribed. Metronidazole is used to treat or prevent pathogenic or anaerobic bacterial infections. The constant accumulation of anti-biotic compounds in the environment, caused by livestock as well as human excreta and urine, has resulted in serious environmental issues.[2,3,23] The decomposition of these compounds in the environment has become a serious issue that must be addressed immediately. Recently in 2022 Wang QQ, Wang DX, Wu YL, Li LX, Sun XY. given review on synthesis of polyoxometalate-based complexes and photocatalytic degradation of metronidazole.[19]new compound, [Cu2(1,10-phenanthroline-5,6-dione)3(PMo12O40)]2·3H2O was synthesized by solvothermal method. The bonding of ligand and metal resulted in a one-dimensional structure. Then, using hydrogen bonding, a two-dimensional layered structure was created. The structures were characterized using X-ray powder diffraction, FTIR, TGA and TG,X-ray photoelectron spectroscopy, and UV diffuse reflectance spectroscopy. In comparison to the conventional

complex, the produced complex had higher purity, yield, thermal stability, and a better band gap.[3] The synthesized complex was employed as a photocatalyst to breakdown metronidazole under UV light, while metronidazole was used as an organic pollutant. The breakdown of metronidazole in the solution will not be aided by changing the pH of the solution. The findings of this research will give basic information for the safe treatment of antibiotic contaminants in wastewater. The degradation of metronidazole under UV light was studied at different ionic strengths and pH levels. The addition of sodium chloride dramatically raised the decomposition rate of metronidazole to 80.2 percent when compared to the original conditions.

Synthesis of [Cu2(1,10-phenanthroline-5,6-dione)3(PMo12O40)]2·3H2O;The single crystal of the complex was synthesized. First,0.0204 g of 1,10-phenanthroline-5,6-dione, 0.0913 g of $H_3PMo_{12}O_{40}\cdot xH_2O$, and 0.0135 g of $CuCl_2\cdot 2H_2O$ were weighed accurately and added to a beaker. Then 10 mL methanol-aqueous solution was added to the beaker, and the mixture 0f solutions was stirred to form a solution. The solution was transferred to the lining of the 25 mL polytetrafluoroethylene reactor and placed in an oven at 150 C for 3 days. The oven was lowered to room temperature at a rate of 5.[19]

Complex	1
Empirical formula	$Cu_4C_{72}H_{36}P_2Mo_{24}N_{12}O_{95}$
Formula weight	5207.83
T/K	296.05
Cryst system	monoclinic
Space group	*P*21/*n*
a (Å)	15.274(2)
b (Å)	22.657(2)
c (Å)	17.824(3)
α (°)	90
β (°)	94.685(8)
γ (°)	90
Z	2
V (Å^3)	6147.6(14)
D_c (g cm^{-3})	2.813
μ (mm^{-1})	3.179
F (000)	0.0523
θ (°)	1.078
R (int)	0.0420
Gof	1.016
R_1 [I >[2d(I)]	0.0527
wR_2 (all data)	0.1421

Table 2; Crystal data and structure refinement for complex [Cu2(1,10-phenanthroline-5,6-dione)3(PMo12O40)]2·3H2O

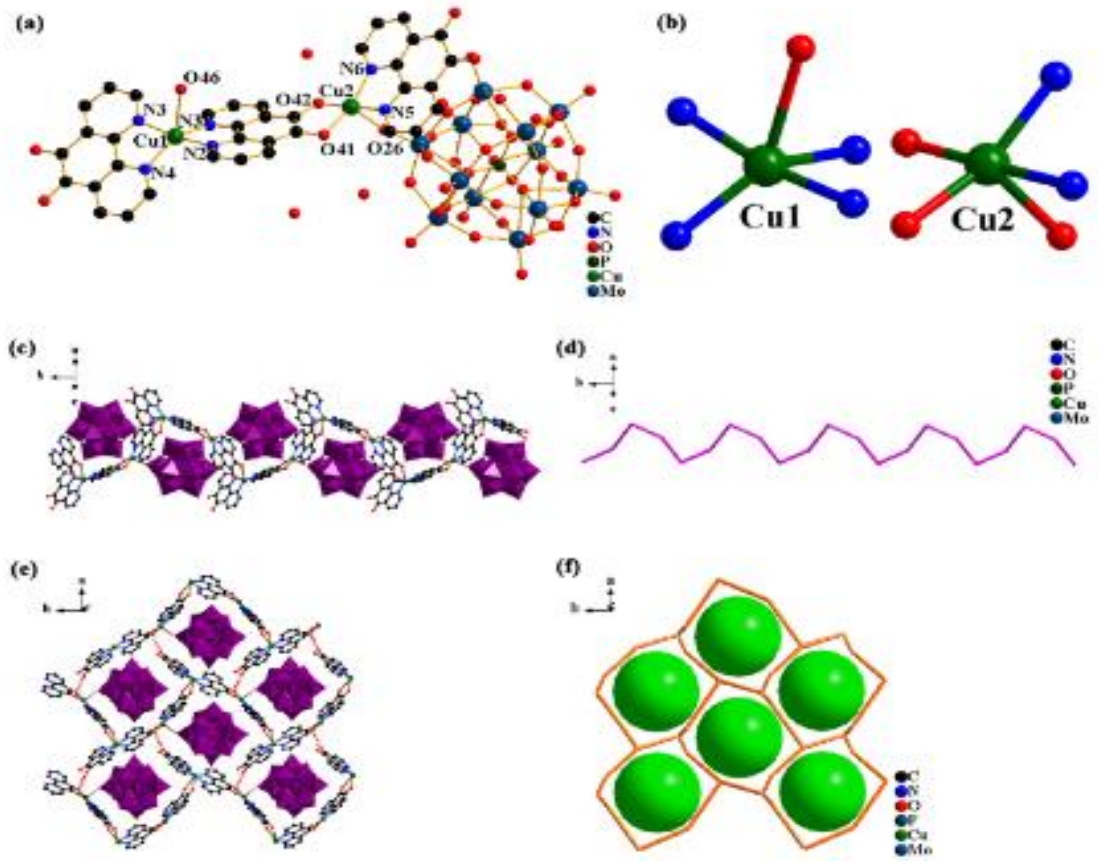


Fig 6; (a) The asymmetric unit of complex 1; (b) Coordination mode of Cu1 and Cu2; (c) One-dimensional structure; (d) Zigzag structure; (e) Two-dimensional structure constructed by hydrogen bonding; (f) [PMo12O40]3-nucleus and polygonal frame[19]

In the photodegradation experiment, the chosen metronidazole (antibiotic pollutant) concentration in the photocatalytic degradation experiment was 30.0 mg. The crystals (catalyst) were then added to 10 mL of the aforementioned solution. For 5 minutes, the solution was ultrasonically dispersed. The solution was adsorption-desorption for 40 minutes in a dark environment. A 250 W mercury lamp was employed as the UV light source to carry out the degradation after the catalysts reached the equilibrium of adsorption and desorption. During the degradation process, a portion of the solution was removed at regular intervals. After centrifugal separation, the samples were analyzed by UV–Vis DRS in the range of 200–600 nm. C/C0 represents the degradation results.[19]

CONCLUSION

Polyoxometalates (POMs) are discrete metal-oxide clusters with unusual photo/electric characteristics that have showed promise as photocatalytic degradation catalysts. The latest progress in the design and synthesis of POM-based photocatalysts, as well as their use in the degradation of organic dyes, pesticides, and other pollutants, are described in this review. From the table1; there are different types of photocatalytic Polyoxometalates are reported out of which tungsten (Agenda atom-W) containing POMs have a photo catalytical activity and these POMs are mainly used in degradation of dyes (such as rhodamine B, methyl orange, methyl red nitrobenzene etc.), water splitting and act as sensor in detection of NH^{4+},NO^{3-}, and $(SO_4)^{2-}$.The most POMs which are studied in this reports are synthesized by a hydrothermal method.

POMs have been demonstrated as a kind of green and economical photocatalyst for the removal pollutants such as medical waste, azo dyes from water/soil, reduction of CO_2 and water splitting from the environment.

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