SYNTHESIS AND EXPLORING THE APPLICATIONS OF METAL-OXO COMPOUNDS

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The Polyoxometalate clusters popularly known as POMs family play a significant role in biological and material science. The recent appearance of number of cited articles including review articles provide insight into the need and necessity of them. The metal oxo compounds investigated in present work have been isolated by using of transition metals such as Mo and W followed by well characterized by employing available analytical instrumentation techniques. In general, POM compounds are attracting research interest because of their simple preparation procedure, thermal stability, various topology, number of coordination modes, easily aqueous soluble in nature and above all cost effective. Some of the targeted applications such as anti-inflammatory, anti-depressant, anti-malarial, anti HIV, anti-microbial, anti-bacterial, anti-fungal, anti-viral, anti-diabetic, herbicidal, larvicidal, anti-skin cancer, insecticidal agents, adsorption, photo degradation, catalysis and sensing studies stimulated the research interest. As an extension on the lookout for the application of POMs, the present thesis work was attempted to explore their specific applications in to biological and materials science.

CHAPTER-I

AN OVERVIEW OF POLYOXOMETALATE COMPOUNDS AND THEIR APPLICATIONS

This chapter deals with general introduction of polyoxometalate compounds with a recent literature review. The polyoxometalate (POM) is very large family of metal-oxo

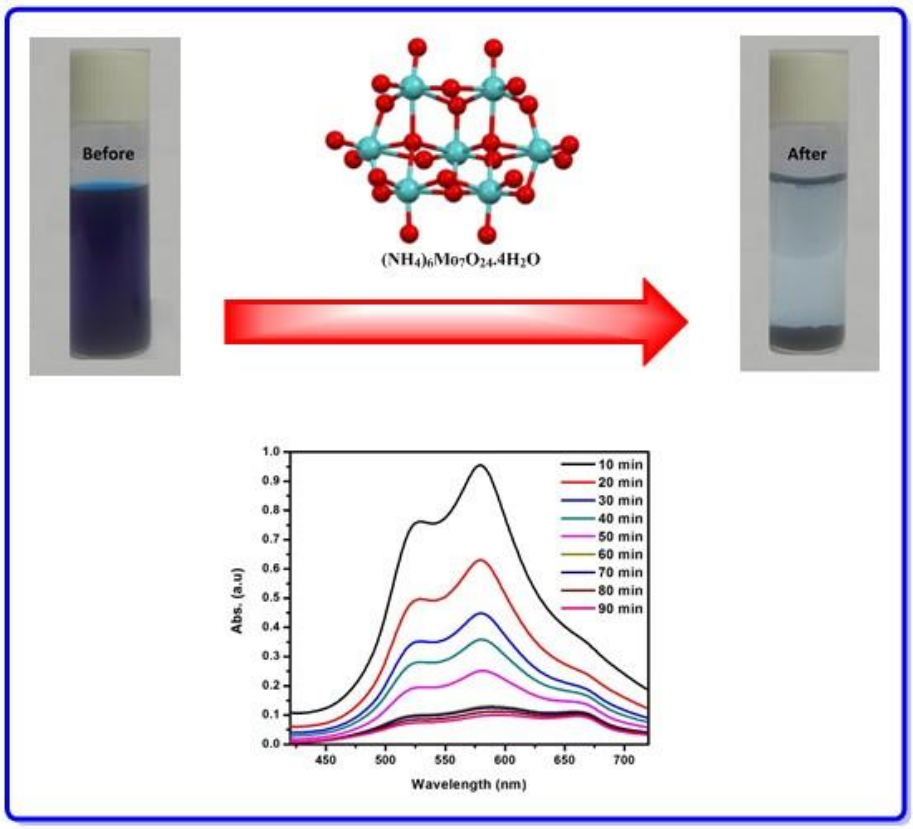
clusters mainly formed by inner transition elements such as Molybdenum (Mo), Tungsten (W), Vanadium (V), Niobium (Nb) and Tandalum (Ta). The metals used to frame metal oxo clusters are otherwise known as 'addenda' atoms. In all the chapter POM compounds are synthesized by the following hydrothermal technique. In the last part of this chapter, the scope of the present investigation has been given.

CHAPTER-II

DEVELOPMENT OF METHYLENE BLUE REMOVAL METHODOLOGY BY ADSORPTION USING MOLECULAR POLYOXOMETALATE: KINETICS, THERMODYNAMICS AND MECHANISTIC STUDY

Molecular polyanion, ammonium heptamolybdatetetrahydrate $[(NH_4)_6(Mo_7O_{24}].4H_2O$ (AHMT) was used to remove methylene blue (MB) dye from an aqueous solution through adsorption technique. Due to an electrostatic interaction of MB cation and AHMT anion adsorption take place. AHMT and MB adsorbed AHMT named as MB-AHMT was characterized by FT-IR, PXRD, SEM and SEM-EDX techniques. Specific surface area (22.175 m^2 g^{-1}) and pore volume (0.059 cm3 g^{-1}) of AHMT was analyzed by BET analysis. The thermal stability and thermal degradation kinetics of adsorbent were assessed by the thermogravimetric curves recorded at different heating rates. The adsorption equilibrium and kinetic studies indicate that adsorption follows with pseudo first order ($R > 0.9998$) rather than pseudo second order. Temperature variation study indicates that adsorption was spontaneous, exothermic and entropy increased processes. Experimental data fitted well with Langmuir rather than Freundlich isotherm with maximum adsorption capacity of 877.19 mg g^{-1}. Excess AHMT was recovered as salt of TBA-AHMT which was characterized by FT-IR spectroscopy. The

investigations indicate that AHMT may be a prospective material for the removal of MB dye from polluted water.

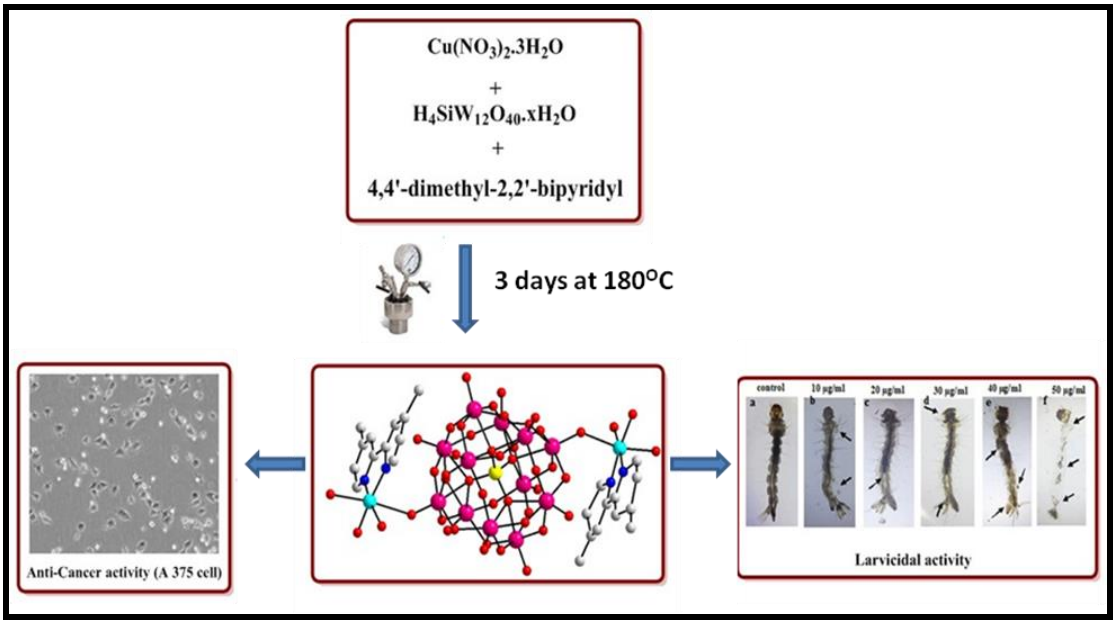


CHAPTER-III

ONE POT SYNTHESIS OF LUMINESCENT POLYOXOMETALATE SUPPORTED TRANSITION METAL COMPLEX AND BIOLOGICAL EVALUATION AS A POTENTIAL LARVICIDAL AND ANTI-CANCER AGENT

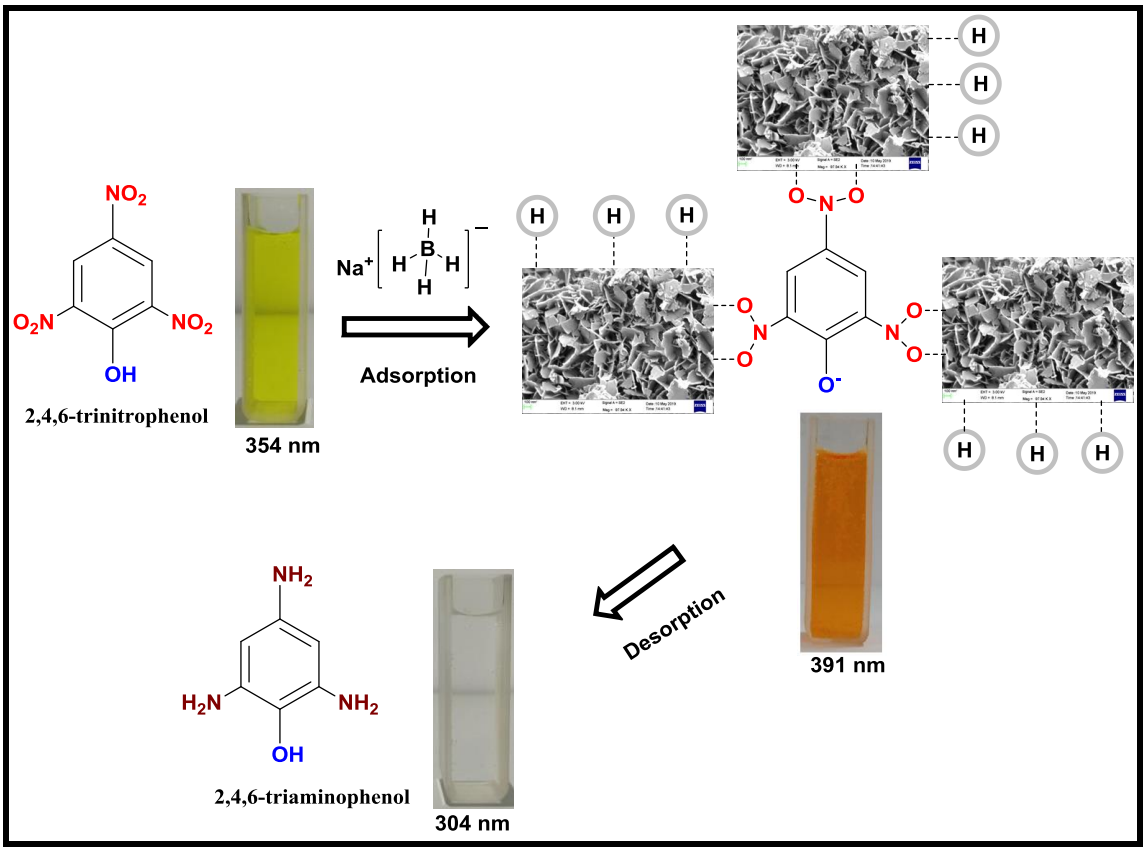
Silicotungstate cluster coordinated organic-inorganic hybrid material $[Cu(dmbpy)]_2[SiW_{12}O_{40}].8H_2O$ (**1**) known as polyoxometalate supported transition metal complex (POM-TMC) was synthesized simply in a one-pot reaction. Larvicidal activity of **1** was investigated against dengue vector *Aedes aegypti*. A series of morphological

changes in the mosquito larva was observed on exposure to different concentrations of the title compound. The total disintegration of the larva was observed at 50 µg/mL. In addition to the larvicidal activity, compound **1** exhibits anti-proliferative activity against the A375 human skin cancer cell line. PXRD pattern stimulated from single-crystal X-ray data was harmonized with PXRD of **1**. Additionally, **1** was characterized by UV-Visible, Fluorescence, UV-DRS, FT-IR and Cyclic Voltammetry. Morphology of **1** was analyzed by Scanning Electron Microscopy (SEM). Composition of **1** was analyzed by Energy Dispersive X-ray SEM-EDX and Elemental analysis.



CHAPTER-IV

POLYOXOMETALATE FUNCTIONALIZED MATRIX MATERIAL: SYNTHESIS, CHARACTERIZATION, REDUCTIVE AND THERMAL DEGRADATION KINETICs



One-pot synthesis of polyoxometalate (POM) based hybrid material **1** was synthesized by mixing copper nitrate, silicomolybdic acid, and urea under hydrothermal condition. The reduction ability of **1** was examined by employing 2,4,6-trinitrophenol (2,4,6-TNP) and 4-nitrophenol (4-NP) in the presence of sodium borohydride in water. The catalytic reduction into the corresponding amine was monitored by UV-Visible spectroscopy (UV-vis). The rate and order of catalytic reduction were studied through chemical kinetics and follows pseudo-first-order. The efficiency of the catalyst was investigated by employing used catalyst **1** for at least ten cycles. Leaching experiments and performance of the reusability of catalyst were supported by FT-IR analyses. In addition, the

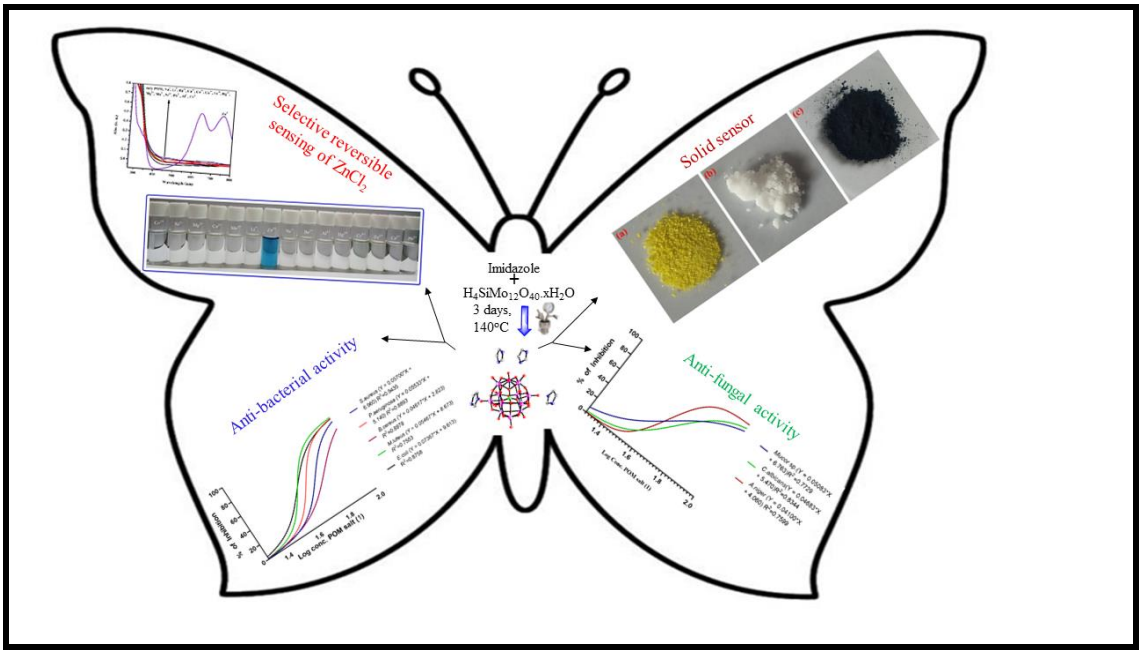
electrochemical reduction ability of catalyst **1** was also executed by Cyclic Voltammetry (CV). Catalyst **1** was characterized by Fourier - Transform Infrared spectroscopy (FT-IR), Powder X-ray diffraction (PXRD), UV-Diffused Reflectance (UV-DRS), Scanning Electron Microscope (SEM), Energy Dispersive X-ray Spectroscopy (EDX), X-ray Photoelectron Spectroscopy (XPS), and Bruner-Emmet-Teller (BET) analyses. Solid-state decomposition kinetics of **1** was performed from Thermogravimetric Analysis (TGA) data by fitting into model equations such as Flynn-Wall-Ozawa (FWO) and corrected (C-FWO).

CHAPTER - V

SELECTIVE AND REVERSIBLE COLORIMETRIC SENSOR FOR $ZnCl_2$: SOLID STATE RECOGNITION AND ANTI-MICROBIAL ACTIVITY OF POLYOXOMETALATE BASED IONIC CRYSTAL

One-pot synthesis of POM-salt (**1**) was achieved by mixing silicomolybdic acid and imidazole in acidic conditions and characterized by FTIR, TGA, SEM, EDX and XPS. The structure of **1** was confirmed by single crystal X-ray analysis. The matching of simulated PXRD pattern with experimental pattern indicates the phase purity of **1**. Interestingly, **1** showed highly selective and sensitive colorimetric detection of zinc chloride ($ZnCl_2$). The addition of $ZnCl_2$ into **1** in DMSO-H_2O mixture showed selective blue colour. In the same way, mixing of $ZnCl_2$ with **1** in solid-state produced blue colour. Other metal ions including other anionic zinc salts did not produce any colour change. The addition of 0.5 μm of $ZnCl_2$ solution resulted in clear blue colour. Similarly, solid mixing of $ZnCl_2$ with **1** can also produce visible colour change. The mechanistic studies indicate that the conversion of Mo^{6+} to Mo^{5+} might be responsible for selective colour change. The reversible colour change between colorless and blue colour upon addition of EDTA into **1**-$ZnCl_2$ and $ZnCl_2$ demonstrate the reusability of **1**. Furthermore, microbial

activity of **1** was investigated towards a series of Gram-positive and Gram-negative bacterial and fungal strains. Effective bactericidal activity of **1** was analyzed against *Staphylococcus aureus*.



CHAPTER - VI

SUMMARY AND CONCLUSION

In summary, the present chapter provides overall outline and conclusion of thesis work. The novel polyoxometalate (POM) clustes investigated in this thesis synthesized by one pot reaction condition and well characterized by various analytical techniques. Furthermore, they were investigated for various applications conclude that they were found as potential material having very good adsorption capacity (Chapter **II**), biological (Chapter **III** and **V**), catalytic (Chapter **IV**) and sensing activity (Chapter **V**). The POM clusters investigated in all the chapters, were synthesized using hydrothermal technique. The hydrothermal technique, once all over again provides evidence to offer simple operational procedure for the preparation of novel material. The protocol of present study may be very much useful for the application of pharmacological and chemical industries as for as material concerned.