CHAPTER 2

Materials and methods

2.1 Chemicals

The chemicals used for all the reactions were reagent grade. The sources of the chemicals are given below:

Acetone, methanol, ethanol, hydrogen peroxide, acetonitrile, ethylacetate, petroleum ether (boiling range 60–80 °C), sodium thiosulphate (RANKEM), diethyl ether, sulfuric acid, sodium hydroxide, potassium dichromate, styrene (E. Merck, India), silica gel (60-120 mesh), boric acid, sodium bicarbonate, potassium iodide, vanadium pentoxide, chitosan (medium molecular weight, deacetylated degree 85%, viscosity 200-800 cps), silica gel (60-120 mesh) (SRL), cyclohexene, L-asparagine (Asn), nicotinic acid (TCI Chemicals (India) Pvt. Ltd.), 5-hydroxy-2-methylfufural (HMF), norbornene, chloromethylated poly(styrene-divinylbenzene) (2.5 mmol g^{-1} Cl loading, 2% DVB) (MR), pyridine, molybdic acid, titanium(IV) chloride solution, 0.09 M in 20% HCl, poly(sodium acrylate) (M_w= 2100), poly(sodium vinyl sulfonate) (M_w = 4000), poly(sodium 4-styrene sulfonate) (M_w = 200000), poly(sodium methacrylate) (M_w= 4000), methyl phenyl sulfide (MPS), methyl p-tolylsulfide (MpTS), ethyl phenyl sulfide (EPS), dimethyl sulfide (DMS), dibutyl sulfide (DBS), butyl propyl sulfide (BPS), dibenzothiophene (DBT), phenylvinyl sulfide (PVS), 2-(phenylthio)ethanol (PTE), dihexyl sulfide (DHS), diphenyl sulfide (DPS), benzyl phenyl sulfide (BPS), allyl phenyl sulfide (APS) were purchased from Sigma-Aldrich Chemical Company, Milwaukee, USA. Merrifield resin was pre-treated with aqueous dioxane (50:50 (v/v)) followed by washing with methanol and dried under vacuum at 90 °C for 8 h before functionalization. Complexes [$MoO(O_2)_2$(sulfonate)]–PS [PS = poly(sodium vinyl sulfonate)] (**PSMo**) and [$Mo_2O_2(O_2)_4$(carboxylate)]–PA [PA = poly(sodium acrylate)] (**PAMo**) were obtained according to the method described in our earlier paper [1-2]. Distilled and deionized water was used for solution preparation.

2.2 Elemental analysis

2.2.1 Molybdenum

2.2.1.1 Gravimetry [3]

Molybdenum was estimated by precipitation as molybdenum oxinate, $MoO_2(C_9H_6ON)_2$ by adopting the following procedure. An accurately weighed amount of the synthesized compounds was dissolved in 20 mL distilled water in a 250 mL beaker

and then acidified with a few drops of dilute sulfuric acid. To the mixture, 5 mL of 2 M ammonium acetate was added and diluted it to 50-100 mL. The solution was then heated up to boiling. The molybdenum was precipitated by the addition of 3% solution of oxine in dilute acetic acid until the supernatant liquid becomes perceptibly yellow. The mixture was then boiled gently and stirred for 3 minutes. The precipitate was then filtered through a constant-weighed sintered glass crucible and washed with hot water until free from the reagent. After washing, it was dried to constant weight at 130-140 ^{o}C.

In case of insoluble peroxidomolybdate complexes immobilized on amino acid or nicotinic acid functionalized Merrifield resin, an accurately weighed amount was ignited in a Bunsen flame to remove the polymer. Subsequently, the residue was acid digested followed by evaporation to dryness. To the dry mass, 20 mL of distilled water was added and then estimated the molybdenum content by following the procedure as mentioned above.

2.2.1.2 EDX analysis, inductively coupled plasma optical emission spectrophotometer (ICP-OES) and atomic absorption spectroscopy (AAS)

Molybdenum content was determined by using Energy Dispersive X-Ray (EDX) analysis, *a*tomic absorption spectroscopy *(*AAS*)* and inductively coupled plasma optical emission spectrophotometer.

2.2.2 Titanium

Determination of the amount of titanium in the compounds was carried out by the use of Energy Dispersive X-Ray (EDX) analysis, inductively coupled plasma optical emission spectrophotometer (ICP-OES) and atomic absorption spectroscopy *(*AAS*).*

2.2.3 Peroxide [4-6]

2.2.3.1 Permanganometry [4]

An accurately weighted amount of a peroxidometal compound was dissolved in a freshly prepared solution of 7 N sulfuric acid containing 4 g of boric acid. To prevent any loss of active oxygen from the solution, boric acid was added which will form perboric acid. The resulting solution was then titrated with a standard potassium permanganate solution.

$$1 \text{ mL of } 1N\ KMnO_4 = 0.01701 \text{ g of } H_2O_2$$

This method is suitable for the determination of peroxide content in case of both peroxidomolybdenum(VI) and peroxidotitanium(IV) compounds.

2.2.3.2 Iodometry [5]

To a freshly prepared solution of 2 N sulfuric acid with an appropriate amount of potassium iodide (~1 g in 100 mL) and 0.5 g of sodium bicarbonate, was added a precisely weighed amount of peroxidometal compound. The mixture was allowed to stand for *ca.* 15 min in the dark in CO_2 atmosphere. The amount of released iodine was titrated against standard sodium thiosulfate solution, a few drops (1-5 mL) of 1% starch solution were added afterwards at near final point. The solution was then turned into deep purple colour and titrated until it became colourless.

$$1 \text{ mL of } 1N\ Na_2S_2O_3 = 0.01701 \text{ g of } H_2O_2$$

This method gives the total amount of peroxide present in the compounds.

2.2.3.3 By standard Ce(IV) solution [6]

An accurately weighed amount of a newly synthesized peroxidometal compound was dissolved in a 0.7 N sulfuric acid solution containing an excess of boric acid. The peroxide percentage of the compound was estimated by titration with standard Ce(IV) sulfate solution was carried out.

2.2.4 Carbon, hydrogen and nitrogen

To determine the carbon, hydrogen and nitrogen percentage present in the compounds, they were analyzed by Perkin Elmer 2400 series II CHN elemental analyzer at the Department of Chemical Sciences, Tezpur University.

EDX analysis was also used to measure the carbon and nitrogen contents.

2.2.5 Chlorine

The amount of chlorine present in the compounds was determined by EDX analysis.

2.2.6 Sodium

Sodium present in the compounds was determined by EDX analysis and ionometer.

2.2.7 Sulfur

The sulfur content in the compounds was determined by EDX analysis.

2.3 Physical and spectroscopic measurements

2.3.1 pH measurement

The pH of the reaction solutions was measured by using an Orion VERSARSTAR pH meter and E. Merck Universal indicator pH 0-14 paper.

2.3.2 Electronic spectra

The diffuse reflectance electron absorption spectra of the solid compounds were recorded by using a Hitachi U-3400 spectrophotometer equipped with diffuse reflectance accessory with an integrating sphere of 60 mm inner diameter and $BaSO_4$ was used as the standard.

The UV-Vis absorption spectra in solution were recorded in a Cary model Bio 100 spectrophotometer with a peltier controlled constant temperature cell, in 1 cm quartz cuvettes. The absorbance values are denoted as, e.g., A_{405}, A_{655} at the indicated wavelengths.

2.3.3 Infrared (IR) and Raman spectra

The infrared (IR) spectra of the compounds were recorded in KBr pellets using a Perkin-Elmer spectrum 100 FTIR spectrophotometer in the range 4000-400 cm^{-1}.

Raman spectra were measured using a EZRaman-N (Enwaveoptronics) that was equipped with a diode laser with an excitation wavelength of 785 nm and a laser maximum output power of 350 mW. The measurement parameters were 10 s exposure time, 5 accumulation, laser power 10% of output power, and a 100X objective. The pixel resolution was set to 1.44 cm^{-1} per pixel.

2.3.4 Surface morphology analysis by Scanning Electron Microscope (SEM)

A JEOL JSM-6390LV scanning electron microscope with an attached energy-dispersive X-ray detector was used to carry out scanning electron microscopy (SEM) and energy-dispersive X-ray analysis of the compound. Scanning was carried out in the 1–20 μM range, and the images were taken at a magnification of 15–20 kV. Data were obtained using INCA software. Standardization of the data analysis is an essential part of the SEM-EDX instrument.

2.3.5 Atomic Absorption Spectroscopy (AAS)

Atomic Absorption Spectrometry was performed in a Thermo iCE 3000 series Atomic absorption spectrophotometer (model analyst 200).

2.3.6 Inductively coupled plasma-optical emission spectroscopy (ICP-OES)

ICP-OES analysis of the compounds was carried out with a Perkin Elmer Inductively coupled plasma- optical emission spectrophotometer, OPTIMA 2100 DV.

2.3.7 Powder X-ray diffraction (XRD)

The powder X-ray diffraction patterns of the compounds were recorded on a Rigaku X-ray diffractometer (Miniflax, UK) at a scanning rate of 10 °C min^{-1} in the 2Θ range 10–70° with the use of Cu Kα (k = 0.154 nm) radiation.

2.3.8 X-ray photoelectron spectroscopy (XPS)

XPS measurements were performed on a Thermo Fisher Scientific X-ray photo spectrometer with an Al Kα (monochromatic) X-ray source. The source was operated at 12 kV and the maintained base pressure in the analysis chamber is $2X10^{-9}$ mbar. The charging of the samples was rectified by setting the binding energy of adventitious carbon (C 1s) at 284.6 eV.

2.3.9 Surface area analysis

The surface areas were measured by nitrogen adsorption/desorption measurements based on the Brunauer–Emmett–Teller (BET) method [7] at 77.3 K on a standard module NOVA 1000E, Quantachrome Instruments. The pore size and pore

volumes were determined by the use of the Barrett–Joyner–Halenda (BJH) model [8] using a NOVA 1000E, Quantachrome Instruments.

2.3.10 ^{1}H NMR spectra

^{1}H NMR spectra were recorded on a JEOL JNM-ECS400 spectrophotometer using deuterated solvents. The chemical shifts are referenced with respect to TMS = δ 0 ppm. The values are given in ppm. The singlet, doublet, multiplet and broad absorption signals were represented by the abbreviations s, d, m and br, respectively.

2.3.11 ^{13}C NMR spectra

The ^{13}C NMR spectra of the solid compounds were recorded using a JEOL JNM-ECX400II spectrometer at a carbon frequency of 100.5 MHz using 1024 X-resolution points, number of scans 544, 5 s relaxation delay and 3.5 ms acquisition time.

For all the water soluble complexes, the ^{13}C NMR spectra were recorded with JEOL JNM-ECS 400 spectrometer at a carbon frequency of 100.5 MHz, 32768 X-resolution points, number of scans 8000-20000, 2.0 s relaxation delay and 1.04 s acquisition time with the ^{1}H NMR decoupling method in D_2O as solvent. The NMR spectra of organic sulfoxides and sulfones were recorded in $CDCl_3$.

2.3.12 GC-MS analysis

GC analysis was carried out with the use of an Agilent 7890A gas chromatograph (GC/GC-MS) with an FID and a 240 ion trap mass detector.

2.3.13 HPLC analysis

HPLC analysis was performed on a Thermo-Scientific Dionex Ultimate 3000 HPLC system equipped with a UV detector.

2.3.14 Thermogravimetric analysis

Thermogravimetric analysis was carried out with the SHIMADZU TGA-50 and Perkin-Elmer STA 6000 system using aluminium pan (heating rate = 10 ^{0}C/min) under an N_2 atmosphere.

2.3.15 Melting point determination

Melting points were measured in open capillary tubes using a Büchi Melting Point B-540 apparatus.

2.3.16 Magnetic susceptibility

Magnetic susceptibilities measurement of the complexes was done by application of the Gouy Method [9], using $Hg[Co(NCS)_4]$ as the calibrant (EMU 50 Magnetometer).

2.4 Computational calculation

Density functional theory (DFT) method was employed for computational calculations. For polymer anchored **pMo** and **pTi** macrocomplexes, DFT calculations were performed on the model complexes using the PWC functional and DNP basis set as implemented in the $DMol^3$ program [10-13].

References

1. Boruah, J. J., Ahmed, K., Das, S., Gogoi, S. R., Saikia, G., Sharma, M., and Islam, N. S. Peroxomolybdate supported on water soluble polymers as efficient catalysts for green and selective sulfoxidation in aqueous medium. *Journal of Molecular Catalysis A: Chemical*, 425:21-30, 2016.
2. Boruah, J. J., Kalita, D., Das, S. P., Paul, S., and Islam, N. S. Polymer-anchored peroxo compounds of vanadium (V) and molybdenum (VI): synthesis, stability, and their activities with alkaline phosphatase and catalase. *Inorganic Chemistry*, 50(17):8046-8062, 2011.
3. Jeffery, G.H., Basset, J., Mendham, J. and Denny R.C. *Vogel's Textbook of Quantitative Inorganic Analysis Including Elementary Instrumental Analysis*, 4th ed., Longman Group Limited, London, pages 472-473, 1978.
4. Vogel, A. I. *A Text Book of Quantitative Inorganic Analysis. Longmans*, Green and Co., New York, page 295, 1962.
5. Vogel, A. I. *A Text Book of Quantitative Inorganic Analysis*. Longmans, Green and Co., New York, page 363, 1962.
6. Vogel, A. I. *A Text Book of Quantitative Inorganic Analysis. Longmans*, Green and Co., New York, page 325, 1962.
7. Brunauer, S., Emmett, P. H., and Teller, E. Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society*, 60(2):309-319, 1938.
8. Barrett, E. P., Joyner, L. G., and Halenda, P. P. The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms. *Journal of the American Chemical Society*, 73(1):373-380, 1951.
9. Chaudhuri, M. K., Ghosh, S. K., and Islam, N. S. First synthesis and structural assessment of alkali-metal triperoxovanadates(V), $A[V(O_2)_3]$. *Inorganic Chemistry*, 24(17):2706-2707, 1985.
10. Hammer, B. H. L. B., Hansen, L. B., and Nørskov, J. K. Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals. *Physical Review B*, 59(11):7413, 1999.
11. Kohn, W. and Sham, L. J. Self-consistent equations including exchange and correlation effects. *Physical Review*, 140(4A):A1133, 1965.
12. Dalley, B. An all-electron numerical method for solving the local density functional for polyatomic molecules. *The Journal of Chemical Physics*, 92(1):508-517, 1990.
13. Delley, B. From molecules to solids with the $DMol^3$ approach. *The Journal of Chemical Physics*, 113(18):7756-7764, 2000.