

Polyoxometalate Nanosorbent for Environmental Remediation

Final Report of

Major Research Project in Science (Chemistry)

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BY

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FINAL REPORT IN BRIEF

This final report consisting of duly filled and signed **Annexure III** (*Report of Work Done*), the consolidated Audited Utilization certificate in **Annexure IV** signed by the Principal of the college, Chartered Accountant, Co-Principal investigator and Principal Investigator, **Annexure V** (*Statement of Expenditure*), **Annexure VI** (*Statement of Expenditure Incurred in Field Work*), and **Annexure IX** (*Proforma for submission of information at the time of sending the final report*) is being forwarded by the Principal, University College, Thiruvananthapuram. The date of commencement of Major Project entitled “**Polyoxometalate Nanosorbent For Environmental Remediation**” is 01-05-2009. The duration of the project is **three years with an extension of six months.**

The investigation aims at environmental remediation with special significance on water pollution management. Environmentally benevolent and effective method to remove water pollutants from aqueous phase is by applying adsorption technique. University Grants Commission, New Delhi-2 provided financial support for completing this research project and we were able to receive the first instalment of Rs. 4,55,300/- on 30-04-2009 through the Principal, University College, Thiruvananthapuram.

Obliging to UGC norms, a committee consisting of the Head of the Department of Chemistry, Principal of the College, Subject Expert, the Principal Investigator and Co-principal Investigator was constituted to select a project fellow. The vacancy of the post of project fellow was published in three leading News Papers of the local area. We received twelve applications and five candidates appeared for the interview of which one candidate was found not eligible since he was over-aged. We conducted the interview in the Principal’s chamber on 21-04-2009 and Mr. S.

Hari Prasad, a first class post-graduate in chemistry with NET, SET and GATE as additional qualifications was selected being the first rank holder of the rank list prepared by the selection committee for the post of the project fellow. (Copy of the proceedings attached). He reported to join duty before the Principal Investigator in the forenoon of the first working day of May 2009. With the silent and encouraging support of the respected Principal, University College, Thiruvananthapuram and the Head of the Department of Chemistry of the same college, the project team carried out the project systematically.

Microcontroller based UV-Visible spectrophotometer (Systronics Model 117) was purchased for improving the quality and convenience of the project in the month of August 2009. Visit to some environmentally significant places, purchase of some useful and good text books for reference and purchase of certain inevitable chemicals are the other activities.

The target to be achieved during the period of the project was the following:

- (i) Literature survey
- (ii) Green strategy for nanosynthesis
- (iii) Nanosynthesis of molybdates
- (iv) Synthesis of nanopolyoxometalates
- (v) Nanosynthesis of mixed-metalates
- (vi) Polyoxometalate synthesis with heteroatom
- (vii) structural elucidation and morphology studies
- (viii) Characterization of environmental samples
- (ix) Kinetic and equilibrium adsorption studies of nanosorbents
- (x) Application of nanosorbents in wastewater treatment

Literature survey is the inseparable part of any research study. Research libraries and World Wide Web service play a vital role in the search of existing

literature. Online Education and Research Centre (OERC) of University College, Thiruvananthapuram provided valuable help for our research work. Simultaneously we carried out nanosynthesis of polyoxometalates. We aimed at the investigation of green strategy for the synthesis. After arriving at the green path of synthesis we synthesized nanomaterials in bulk.

Phosphomolybdate in the nano level was our first product. We proceeded with tungstates and vanadates. Then we substituted phosphorus with sulphur or arsenic. We continued with the synthesis of polyoxometalates containing more than one kind of metal and synthesized mixed-metalates in the nano level.

The nanopolyoxometalates were characterized by various techniques and the morphology of each sample was studied separately. Then we concentrated our studies to elucidate the way of changing the morphology. The way of agglomeration and structural details were our next part of the study. The application of nanomaterials also deserve a special significance. So we continued our investigation to find out the efficiency of these new chemicals to function as adsorbent for dissolved pollutants present in the aqueous phase and came to the conclusion that they are suitable adsorbents for toxic heavy metal ions.

The water samples were collected periodically and analyzed using standard methods. These environmentally significant sites belong to Thiruvananthapuram, Kollam and Ernakulam districts of Kerala state. We visited different places in Kerala state, which seem to be environmentally significant. Since a number of industries are located in the district of Ernakulam, we visited some pre-determined spots of this district to investigate the water quality. We extended our studies to Vellayani and Chavara

The district of maximum height from sea level in Kerala is Wynad. We planned to observe and investigate the water samples of a few places in Menangadi area of Wynad district.

Our next visit was to Thrissur district. Surface water samples were collected and tested in order to assess their suitability for human consumption.

A number of water pollution studies were initiated in Kozhikode district. The water quality of the river Chaliyar was studied by different agencies and voluntary organizations. We went to West Hill and water samples of certain selected areas of West Hill were made the object of our study.

We planned to associate our work with the Environmental Science Department of Cochin University of Science and Technology by exploiting their laboratory, library and instrumental facilities. We visited the department and some neighbouring places of the University to collect samples for our investigation.

Our next visit was to Palakkad district. We gave special attention to the industrialized sector and water samples from Kanjicode were subjected to intensive study.

Kollam is a coastal district near to Thiruvananthapuram. Chavara was selected to be our experimental spot considering the presence of an industrial firm namely Kerala Metals and Minerals Ltd., Chavara.

There is a place in the Ernakulam district where aquaculture is promoted. Hectares of land is used for aquaculture in the area of Kadamakudi. Many people earn their lively-hood from this cultivation. So water samples were collected from that local area, which seems to be environmentally important.

In order to assess the quality of our work we collected opinion from the experts of the Environmental Studies Department of Cochin University.

Water samples of Kadamakudi area in Ernakulam district were collected to note the changes in the qualities of water samples especially the contents of inorganic and organic pollutants due to seasonal variations.

Kalamassery was the next centre of sample collection since it was close to the industrial belt of Cochin area. Analysis of water samples and the removal of pollutants by using nanosorbents were investigated.

Kunnamkulam of Thrissur district attracted our attention and we collected samples of water from there and analyzed to detect the presence of pollutants.

The effect of seasonal changes of Meenangadi and its influence in the quality of water was measured for updating the information relating to that area.

Kanjicode is the industrial area of Palakkad district. Since the extent of industrialization is directly proportional to water pollution, water samples from Kanjicode area were examined.

Chavara of Kollam district is one of the selected sites from where water samples were collected periodically in addition to Vellayani lake of Thiruvananthapuram district and Cochin industrial belt of Ernakulam district.

Some selected sites were visited and samples for investigation were collected from Cochin industrial belt by halting at Kalamassery in Ernakulam district.

Kalpetta is another hill area, which is the district head quarters of Wynad district. Water samples of Kalpetta being significant, attempts were made to analyze in order to study the composition of ground water in the micro and macro level.

It was felt that without analyzing the water samples of Guruvayoor area this project will remain incomplete. So water samples from Guruvayoor area were also subjected to investigation. We completed our field work by visiting Kadamakudi again.

We limited our detailed studies on three important places listed below. From these environmentally significant selected sites water samples were collected periodically for analysis:

(i) Vellayani lake in Thiruvananthapuram District : seems to be contaminated with organic and inorganic pollutants.

(ii) Kerala Metals and Minerals Ltd., Chavara in Kollam District : polluted with light metal ions and heavy metal ions

(iii) Cochin industrial belt in Eranakulam District: contaminated with heavy metal and many other toxic pollutants.

Nanosyntheses were also carried out in the laboratory. DPC was used as the surfactant. Studies were conducted by varying the concentration of the surfactant, contact time, temperature, stirring speed, stirring interval and reactant concentration. Under optimum conditions the samples were prepared and subjected to characterization and environmental application.

The fifteen nano samples synthesized for the present project are:

1. Nanophosphovanadate (PVO)
2. Nanosulphovanadate (SVO)
3. Nanoarsenovanadate (AVO)
4. Nanophosphomolybdate (PMO)
5. Nanosulphomolybdate (SMO)
6. Nanoarsenomolybdate (AMO)
7. Nanosulphotungstate (SWO)
8. Nanophosphotungstate (PWO)

9. Nanoarsenotungstate (AWO)
10. Nanophosphomolybdotungstate (PMWO)
11. Nanosulphomolybdotungstate (SMWO)
12. Nanoarsenomolybdotungstate (AMWO)
13. Nanosulphophosphomolybdate (SPMO)
14. Nanosulphophosphotungstate (SPWO)
15. Nanoarsenosulphomolybdate (ASMO)

Collection and characterization of environmental samples and synthesis of fifteen nanosorbents were completed and reported in the second annual report. The adsorption capacity of the nanosorbents is to be evaluated and studies are to be conducted in the direction of improving their adsorption capacity. The derivatives of these sorbents with more functionality may serve the purpose. Nanopolyoxometalates are expected to be good adsorbents for heavy metal ions. Here we measured the efficiency in the treatment of aqueous environmental samples containing heavy metal ions. We elucidated optimum conditions under which maximum adsorption of heavy metal ions took place. The removal of each metal ion was conducted separately for which synthetic wastewater samples containing Hg(II), Pb(II), Cd(II), As(III), Bi(III), Mo(VI) and Cr(VI) and artificial effluents were prepared and they were treated separately with each nanosorbent. Then mixed solutions were prepared and they were also treated separately with individual nanopolyoxometalate and studied the adsorption isotherm of binary solute system. Water samples collected from selected sites, wastewater samples synthetic effluents, industrial effluents and spiked industrial effluents were treated with nanosorbents in order to evaluate the efficiency of each

nanosorbent and hence to assess the utility of the nanosorbent in wastewater treatment. The results are in good agreement with those obtained in the batch experiments.

Mr. Hari Prasad joined doctoral research under the guidance of the Principal Investigator of this project (Ref:- U.O. No. Ac. E1B2/33654/2010 Dated 27-09-2010) after resigning the post of project fellow. Immediate steps were taken for the selection of another suitable project fellow observing UGC norms to fill up the vacancy of project fellow for which the whole selection process was repeated. This was informed to UGC in time. Then steps were taken to appoint Mrs. S. Hema in the existing vacancy of the project fellow and issued the appointment order. Mrs. S. Hema reported to join duty before the Principal Investigator in the FN of first November 2010. She carried out the duties punctually, systematically and regularly.

Synthesis and characterization of nanopolyoxometalates of Tungsten, Vanadium and Molybdenum were continued. Due to financial crisis the work was delayed to a certain extent. However, we presented the Mid-term report before the expert committee at New Delhi on 13th March 2011. Our request for the extra grant was favourably considered and we got an extra fund of Rs. 15000/- along with the second instalment which was encashed on 07-10-2011 (7th October 2011). Our project work was accelerated as soon as we received the second instalment of Rs. 5,89,000/-. Then we requested for an extension of six months duration without additional financial support. That request was also considered favourably and our attempt to finish the project work within October 2012 was successful.

The account corresponds to the expenditure upto 30-04-2012 because the extension requested was without financial support. We continued the project work with the hope that we can publish a few more research papers. At present there are four Published works and two under publication in reputed national and international

journals. Prof. G. Rajeev (Co-principal Investigator), Dr. M. K. Sreedhar (Principal Investigator), Mr. S. Hari Prasad and Mrs. Bessy D'cruz (Research Scholars), S. Hema (Project Fellow), B. N. Jisha, R. Remya, Sarika R. Nair, E. P. Jessy, C. P. Drisya, Vandana G. Krishnan and K. V. Sanal (*Postgraduate Students*) participated in this research programme. The venue was the Research Department of Chemistry, University College, Thiruvananthapuram with the financial support of University Grants Commission, New Delhi and it is expected that we will proceed with the work even after the expiry of the project period since the research is environmentally more significant and beneficial for the society.

Air, earth and water are the three essential components without which man cannot survive. Due to human interaction, the atmosphere, lithosphere and hydrosphere are becoming more and more polluted. Here the humble attempt of the project team is to save hydrosphere and we recommend adsorption as the most promising technique for the effective removal of many dissolved pollutants found in water. Nanopolyoxometalates were found to be good adsorbents for heavy metal ions. Many oxometalates are soluble in water, but nanopolyoxometalates are insoluble in water and behave as good adsorbents for heavy metal pollutants present in aqueous phase.

The results of the study were published through paper presentation in National / International seminars and also by sending research papers to National / International journals.

The synthesis and characterization of nanophosphomolybdate was presented in "*Spectrum-2009*" held at Thiruvananthapuram in which almost all research departments of Kerala state participated.

Heavy metal pollutants cannot be degraded and detoxified biologically. So we attempted the removal of pollutants by adsorption technique. Instead of nanosorbents

we used a naturally occurring adsorbent viz. *Phyllanthus emblica* powder with the aim of comparing its efficiency with that of nanosorbents. These results were presented in a National Seminar convened by Indian Council of Chemists held at Patan in Gujarat in November 2009.

Naturally available adsorbent after surface modification was used in the removal of mercury from aqueous solution. The observations were analyzed and interpreted and presented in an international conference held at Vellore, Tamil Nadu in December 2009 under the auspices of Indian Chemical Society.

Kerala Science Congress-2010 review committee accepted our paper entitled “*Green Chemical Paths for polyoxometalate nanosynthesis*” and published in the proceedings of 22nd Kerala Science Congress convened at KFRI, Thrissur in January 2010

We got another opportunity to present another paper entitled “*Surfactant controlled Synthesis of Nanosulphovanadate*” in the international seminar on nanotechnology and nanomaterials : current status and emerging trends in February 2010 at Irinjalakkuda.

Green chemical paths in the synthesis of nanomaterials is very significant and challenging work in nanoscience and technology. Green Synthesis of nanosulphovanadate and its application in the removal of arsenic was presented in the national conference held at Bharathiyar University, Combaitore in December 2010.

In connection with the celebrations of International Year of Chemistry we participated in the Chennai Chemistry Conference-2011 held at IIT Madras by presenting a paper on “*High Performance Nanophosphomolybdate for the Removal of Mercury from Water and Wastewater*” in February 2011.

The paper entitled “*Sorption and separation of Bi(III) from aqueous system by using nanosulphovanadate*” was presented by the Principal Investigator in the Annual

Convention of Chemists and Celebration of International Year of Chemistry in December 2011 at the University of Allahabad, Uttar Pradesh as a part of the Annual Convention of Chemists convened by Indian Chemical Society.

The article regarding the role of arsenomolybdate in the removal of Mo(VI) was presented by the project fellow in the National seminar on Frontiers in Chemistry convened by the Department of Chemistry, University of Kerala in April 2012. The paper entitled "*Kinetic and Equilibrium Modeling of Mo(VI) Adsorption onto Nanoarsenomolybdate*" concluded by pointing out that the overall process of adsorption is spontaneous and endothermic. The regeneration of this nanosized adsorbent was also possible.

The Co- principal Investigator of this Major Research Project was also kind enough to present a paper entitled "*Green Synthesis of Nanophosphosulphotungstate for Environmental Remediation*" in the three day national seminar convened by the Department of Chemistry, University of Kerala, Thiruvananthapuram in April 2012 since the actual duration of the project was only upto 30-04-2012.

The nanopolyoxometalates synthesized are to be studied computationally. Initially we attempted to study *ene* reaction. Being a new attempt we were able to publish a paper on computational chemistry entitled "*Reaction co-ordinates of Ene Reaction in Configuration Space*" in the *Journal of Ultrachemistry* in June 2012.

The project was totally wound up in the afternoon of 31-10-2012 (Wednesday) after a brief concluding session in which the Head of the Department of Chemistry, University College, Thiruvananthapuram presided, Principal Investigator welcomed, Co-principal Investigator, faculty members in Chemistry, research scholars and PG students participated. All assets earned through this project were handed over to the college through the Head of the Department of Chemistry. These assets were taken in the stock and necessary entries were made in the stock register and a proper receipt

was issued by the Head of the Department countersigned by the Principal, University College, Thiruvananthapuram.

We got an opportunity to publish the next research paper on sulphovanadate nanospheres, which were the aggregation of particles of diameter below 10 nm in *Asian Journal of Chemistry* in October 2013.

Synthesis and characterization of sulphomolybdate was communicated to a reputed international journal namely *Bulletin of Material Science*. The paper, which discusses the reaction parameters and the mechanism of agglomeration was accepted and then published in November 2013.

New journal of Chemistry is a reputed international journal, which accepted and published our paper on cetylpyridinium phosphotungstate in September 2014. The paper discusses the green synthesis of Cetylpyridiniumphosphotungstate nanospheres, its characterization and photocatalytic activity.

Adsorption being a method for environmental remediation, systematic study was initiated with a relatively cheap adsorbent and the observations were interpreted and send to the *Journal of Council of Chemists* for publication.

In October 2014 we communicated our next paper entitled “*Green Synthetic Evolution of Crystalline Arsenotungstate Nanospheres and Nanocapsules*” to *Materials Characterization*, which is an international journal published from USA.

MATERIALS AND METHODS

All the reagents and solutions were prepared with Chemicals of analytical reagent grade from Fluka (Switzerland), BDH (UK), Merck (Germany) and E Merck (India) and deionized water with specific conductivity less than $1.0 \mu\text{S cm}^{-1}$ at 303 K. Sodium molybdate (AR) as the source of molybdenum and dodecyl pyridinium chloride (DPC) as surfactant were used in the synthesis of nanopolyoxometalates.

Particle size analysis was done on a *Malvern-ZE tasizer Nano ZS Particle Size Analyzer*. Sub micron particle sizes are measured by observing the scattered light from these particles, determining the diffusion speed and deriving the size from this using Stokes-Einstein relationship. This method is called Dynamic Light Scattering. Modern electronic digital voltmeter scaled pH meter, magnetic stirrer and borrowed instruments were used for characterization. The water samples collected from selected sites were analyzed to measure dissolved oxygen (DO), COD, BOD, Phenols, Phosphates, Nitrates, Chloride, heavy metal ions, ammonium and suspended solids applying standard methods. Microcontroller based UV-Visible spectrophotometer (Systronics Model 117) was used for UV-analysis of the synthesized samples.

FTIR studies were conducted on Shimadzu Spectrophotometer at room temperature using KBr pellets in the range of $4000 - 400 \text{ cm}^{-1}$, thermal analysis was performed on Universal V3.9A TA from $293 - 1263 \text{ K}$ at a heating rate of 10° C/min . in nitrogen atmosphere. X-ray diffraction data were recorded on X'pert software diffractometer. In addition to Scanning Electron Microscopy, High Resolution Transmission Electron Microscopic studies were done on Philip's CM 20 electron microscope. The Atomic Force Microscopic study was done by dispersing the sample in absolute alcohol and deposited on a silicon substrate using the principle of cantilever. Borrowed instruments from other institutions were also used for EDX and ICP-AES for the characterization of the newly synthesized nanochemicals.

CONCLUSION

The Major Research Project entitled "*Polyoxometalate Nanosorbent For Environmental Remediation*" (Ref: F. No. 35-144/2008 (SR) Dated 20-03-2009 / 10-08-2011) was carried out in the research laboratory, Department of Chemistry, University College, Thiruvananthapuram with the financial support of University Grants Commission, New Delhi. The project was of three year duration with an

extension of six months. This bound volume is the Final Report for the period of 01-05-2011 to 31-10-2012. During the first year of the project we were engaged in the characterization of the environmental samples collected from selected sites. Green methods for the synthesis of the nanophosphomolybdates were investigated. We continued our study by synthesizing nanomolybdates, nanovanadates, nanotungstates, nanomixedmetalates and nanometalates with substituted heteroatoms. The nanopolyoxometalates synthesized in our laboratory were used for the treatment of synthetic effluents and industrial wastewater containing toxic heavy metal ions. The samples of water were collected from environmentally significant selected spots within the state of Kerala. The adsorption studies show that the newly synthesized nanosorbents are efficient adsorbents with very high removal capacity of pollutants from aqueous phase and the nanosorbents may be regenerated for fresh application. Synthesis, characterization and environmental application of nanosorbents are the outcome of this research project. As the outcome of this Major Research Project, there are fifteen publications. The list of publications is furnished as a table in Annexure IX and reprints/preprints are attached. The e-copy and the hard copies as bound volumes were submitted to the Principal, University College, Thiruvananthapuram for the onward transmission to University Grants Commission, New Delhi.