International Research Journal of Engineering and Technology (IRJET) e-ISSN: 2395-0056
Volume: 11 Issue: 01 | Jan 2024 www.irjet.net p-ISSN: 2395-0072

Sensor applications of NPs using Cyclic Voltammetry: A Review

ARATI C[1], PRAVEEN. B M[1,*], PAVITHRA B N[1,2], SUDHAKAR[3]

[1] Department of Chemistry, Srinivas University, Institute of Engineering & Technology, Mukka, Srinivas Nagar, Mangaluru, Karnataka, India.
2 School of Engineering, Department of Chemistry, Presidency University, Itgulpura, Bengaluru, Karnataka, India.
3 Department of Chemistry, Raja Rajeswari College of Engineering, Ramohalli Cross, Kumbalagodu, Bengaluru, Karnataka, India.

---***---

Introduction

The global concern of water pollution caused by various contaminants originating from wastewater, agriculture, municipalities, and industries is well known. These pollutants, found in unbalanced concentrations, pose serious threats to human health and aquatic life.

Industrial waste is being discharged into the environment at an increasing rate due to the development of the chemical industry. It is projected that this waste will have a deleterious effect on human immunity and reproduction, leading to neurological and behavioral disorders in people. Since there is currently no cure or therapy for many diseases, like diabetes, it is crucial to manage the disease's symptoms. Blood glucose monitoring is thought to be a crucial tool for both early disease detection and management of its side effects. Furthermore, blood glucose monitoring might be highly beneficial for the treatment of patients. As a result, developing new sensors has emerged as a crucial area of research for the detection of substances at trace amounts. Researchers worldwide are actively exploring measures and detection methods for these pollutants and detecting biological molecules.

Researchers have been working on the use of nanostructures that can sense these pollutants and biomolecules accurately and specifically. To address these challenges, researchers are exploring innovative nanomaterials, such as metal oxides, and doped metal oxides.

Compared to other conventional methods, electrochemical detection techniques have advantages. One of the industries with the quickest growth is electrochemical sensors. Amperometric sensors generate an electroactive species by the oxidation or reduction of measuring the voltage differential between an electrode and a reference.

Cyclic voltammetry (CV) is an electrochemical method used in the study of redox processes, and electron transfer chemical reactions. Studying chemical reactions triggered by electron transfer, such as catalysis, is aided by it.

CV gives the analysis of current (i) as a function of applied potential (V)

The applied potential measures the concentrations of redox species at the electrode surface. The Butler-Volmer or Nernst equations explain the rate of reaction.

$E=E^0-RT/nF \ln [C_R^0/C_O^0]$ .... Nernst equation

CR(0,t)e(1-α) nf/RT(E-E0) - CO(0,t)e –αnF/RT(E-E0)] = nfAk0* i...The Butler-Volmer formula .

The Nernst equation helps to understand the system's behavior during cyclic voltammetry experiments. The system's respond depends on changes in concentration or electrode potential. The "duck" shape is a result of the processes at the electrode interface.

The stability of the analyte is predicted by the Chemical reversibility of reduction and reoxidation. Electrochemical reversibility refers to fast electron transfer kinetics between the electrode and analyte, following the Nernst equation.

Peak-to-peak separation (ΔEp) is used to assess reversibility, with a value of 57 mV at 25 °C indicating reversible electron transfer.

Nanomaterials, characterized by their nanoscale dimensions, offer unique physicochemical properties that make them highly attractive for a wide range of applications across various fields. The advantageous properties of nanomaterials are primarily attributed to their large surface-to-volume ratios and quantum effects, enabling improved and tailored properties. Nanomaterials are utilized in the development of highly sensitive and selective chemical sensors for detecting gases, pollutants like heavy metals and also biomolecules.

2. Electrochemical cell used for cyclic voltammetry experiments.

Key components and their roles:

1. Working Electrode

This is the location of the relevant electrochemical reaction. Usually, it is composed of the subject matter being studied. The working electrode is central to the experiment, and its characteristics are crucial for data collection.

2. Counter Electrode:

The counter electrode is essential to complete the electrical circuit.

It doesn't participate in the electrochemical reaction but facilitates the flow of electrons. Typically, it is made of an inert material like platinum. To maintain a constant potential, the surface area of the counter electrode needs to be significantly greater than that of the working electrode.

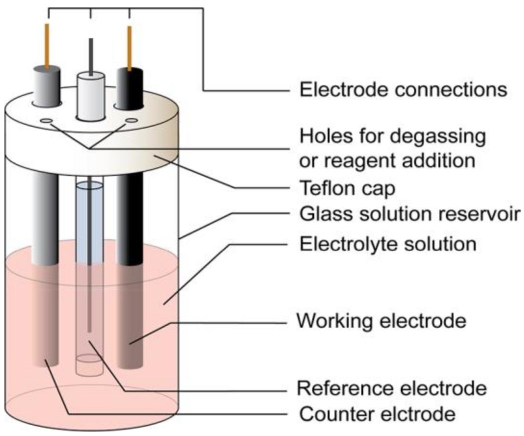


Fig. 1. Schematic representation of electrochemical cell

3. Reference Electrode:

The reference electrode is crucial for measuring and maintaining a stable and known electrochemical potential. It is usually a reversible electrode with a well-defined redox potential, such as a silver/silver chloride electrode. To guarantee the accuracy of the recorded data, the potential of the working electrode is monitored in relation to the reference electrode.

4. Electrolyte:

The electrolyte is the medium through which ions are transported between the working and counter electrodes. It's typically a solution containing the species of interest. The choice of electrolyte can have a significant impact on the reaction kinetics and the behavior of the electrochemical cell.

5. Cell Body/Container:

The electrochemical cell is contained within a vessel or cell body, which is usually made of chemically inert materials such as glass or plastic. It separates the working and counter electrodes and holds the electrolyte. The design of the cell body is crucial to prevent contamination and maintain a controlled environment.

In this review we are discussing the investigation of sensing ability of various nanoparticles towards different heavy metals, rare earth metals and biomolecules.

3. Methodology:

The nanoparticles to be used as a sensor is made as working electrode in the construction of electrochemical cell. This prepared working electrode; reference electrode and counter electrode are connected to the CV instrument and cyclic voltammograms are studies for the applications of NPs as a sensor.

Electrode Preparation by using Carbon Paste:

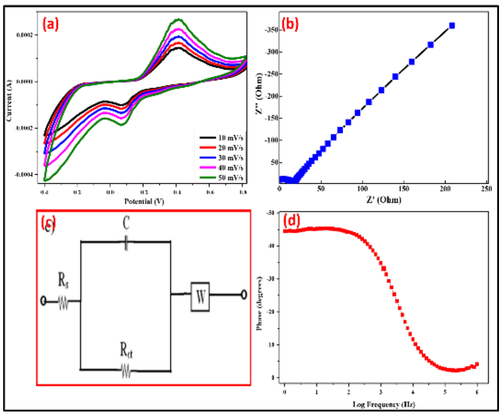
In most of the research working electrode is prepared as follows:

To form the carbon paste electrode (CPE), the generated sample NPs, silicon oil, and graphite powder were ground (hand mixed) in a mass ratio of 15:15:70 for about half an hour. The mixer was then put inside a microtip tube. The exterior of the cavity tube was polished until it was level with a piece of weighing paper.

4. Investigation of various Nanoparticles as a sensor

H.V. Harinia *et al*: Synthesized nanomaterial, $Cu_2ZnAl_2O_4$ (CZA), sensing ability investigation was conducted in a solution containing 1 N KCl. The synthesized CZA nanomaterial exhibited exceptional redox reaction properties

The synthesized CZA nanomaterial exhibited remarkable sensitivity and selectivity in the detection of lead and tin ions. This underscores its potential as a highly efficient sensor for heavy metal detection, which is crucial in environmental monitoring and industrial application.



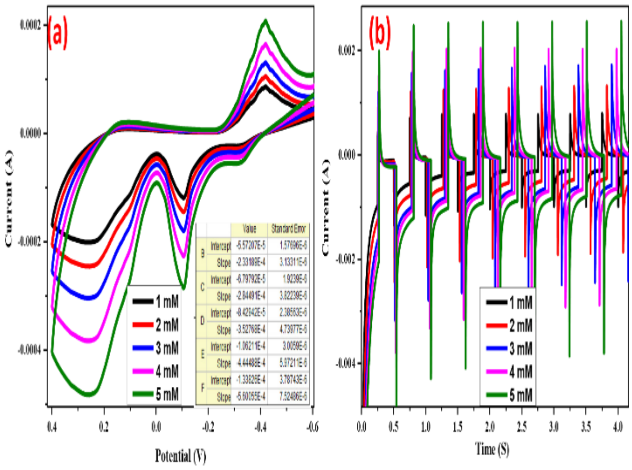


Fig. 2. a) CV plot, b) EIS spectra, (c) resulting circuit model and (d) Bode plot of modified CZA electrode.

Fig. 3a) CV plots of CZA NPs demonstrating lead detection and b) curve of amperometry during lead sensor.

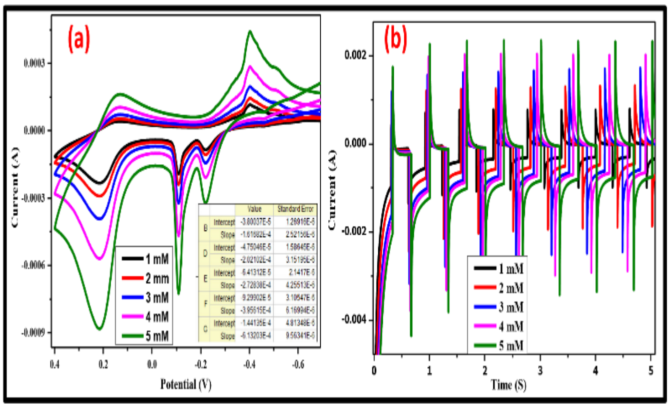


Fig. 4. a) CV plots of CZA NPs demonstrating Tin detection and b) curve of amperometry during tin sensor

$Cu_2ZnAl_2O_4$ (CZA) nanoparticles showed ability to detect lead and tin ions at concentrations of 1 mM (millimolar). The study reveals a rapid reaction time of 3 seconds for the electrode material. applications where rapid monitoring is required.

Improved lead and tin metal ion sensing potential was demonstrated by the CZA-modified electrode. This indicates that the CZA nanostructure enhances the sensitivity and selectivity of the electrode towards the target metal ions.

A. Naveen Kumar *et al:*

Synthesized $La_{10}Si_6O_{27}:RE^{3+}$ (RE = Eu, Sm, Dy, Tb) nanophosphors (LNPs) and investigated its application in electrochemical sensing, for paracetamol. The rare earth ions (Eu^{3+}, Sm^{3+}, Dy^{3+}, and Tb^{3+}) were doped into LNPs at a concentration of 5 mol%. The dopants enhanced the electrochemical sensing characteristics, making the LNPs more promising for sensor applications.The modified LNP electrodes were successful in sensing paracetamol in an acidic media. For medicines with a 1 mM concentration, a 3 second response time suggests the possibility of sensitive and swift detection.

Table1: Estimated particle size (nm) of $La_{10}Si_6O_{27}:RE^{3+}$ (5 mol%) NPs for (211) plane

Samples	*Planes*	*Particle sizes (nm)*
$La_{10}Si_6O_{27}:Eu^{3+}$ (5 mol%)	*(211)*	*0.274*
$La_{10}Si_6O_{27}:Sm^{3+}$ (5 mol%)	*(211)*	*0.275*
$La_{10}Si_6O_{27}:Dy^{3+}$ (5 mol%)	*(211)*	*0.280*
$La_{10}Si_6O_{27}:Tb^{3+}$ (5 mol%)	*(211)*	*0.273*

An efficient and widely used antipyretic and analgesic is paracetamol. It is commonly used as an over-the-counter medication to treat a number of illnesses, such as headaches, pain, fever, arthritis, and colds.

Detection and monitoring Paracetamol are crucial for preventing and diagnosing overdose situations, ensuring that individuals take the medication within recommended limits.

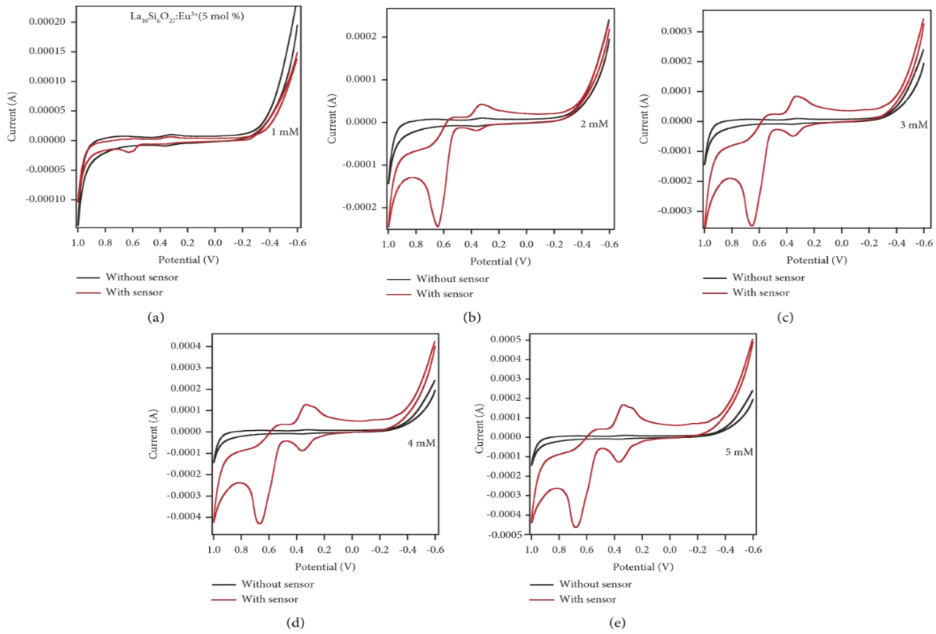


Fig. 5. a) CV plots of $La_{10}Si_6O_{27}:Eu^{3+}$ with and without sensor.

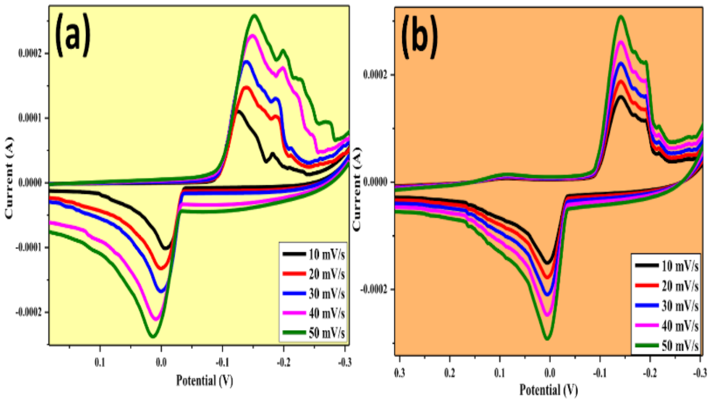
The study holds significance in providing a simple, rapid, and portable method for detecting and monitoring paracetamol levels.

The application of electrochemical sensors, particularly voltammetry, adds to the existing arsenal of techniques for drug quantification.

Table 2: Peak appearance at different potentials when employing the La10Si6O27 electrode material with different dopants to detect paracetamol

Sample names	Oxidation peak potential (V)	Reduction peak potential (V)
$La_{10}Si_6O_{27}:Eu^{3+}$ (5 mol%)	0.62, 0.37	0.34
$La_{10}Si_6O_{27}:Sm^{3+}$ (5 mol%)	0.78, 0.51	0.48
$La_{10}Si_6O_{27}:Dy^{3+}$ (5 mol%)	0.62, 0.35	0.34
$La_{10}Si_6O_{27}:Tb^{3+}$ (5 mol%)	0.6, 0.62, 0.36	0.32

Produced lanthanum oxide (La2O3) nanoparticles utilizing Tridax (T-La_2O_3) and Centella asiatica (C-La_2O_3) leaf powders using a green combustion method.The electrochemical behavior of the La_2O_3 nanoparticles was studied, to investigate the sensing ability for paracetamol using CV techniques. Results showed excellent sensing ability of the synthesized NPs.



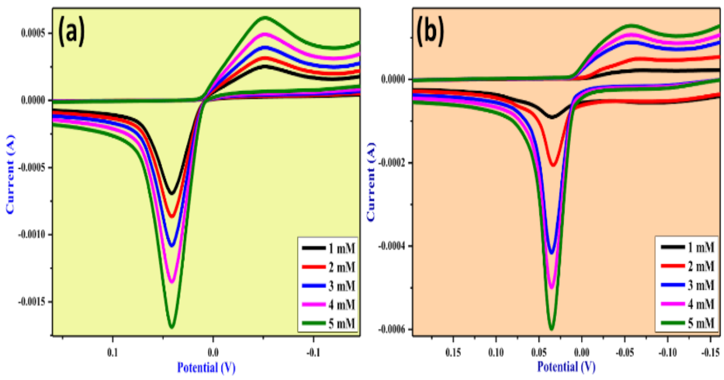


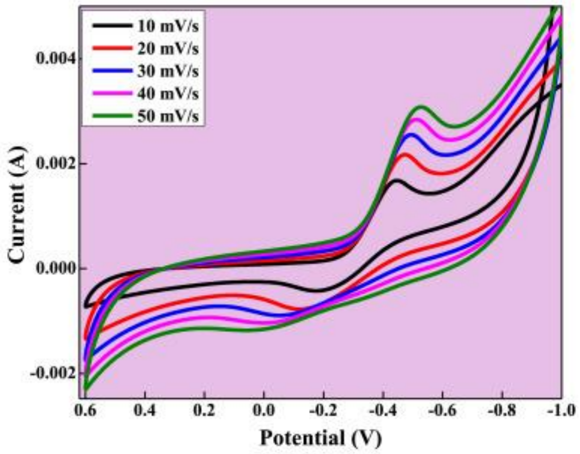
Fig. 7. Paracetamol cyclic voltametric sensing (1–5 mM)

Fig. 6. Cyclic Voltammogram of

(a) *C*-La_2O_3 and (b) *T*-La_2O_3 NPs v/s Ag/AgCl electrode using (a) *C*-La_2O_3 and (b) *T*-La_2O_3 electrodes in 1 M KOH electrolyte

Examined sensing applications for the detection of hazardous elements like lead as well as the production and characterisation of molybdenum oxide nanoparticles (MoO_3 NPs) utilizing a green combustion process with powdered Centella asiatica plant.

The capability is tested in basic medium. The electrode, composed of MoO_3 (Molybdenum trioxide), shows shift in both oxidation and reduction curves in the presence of lead, indicating its suitability for lead sensing. The oxidation peak shifts towards a positive potential, results in a peak value of 0.14 V that increases with higher lead concentrations



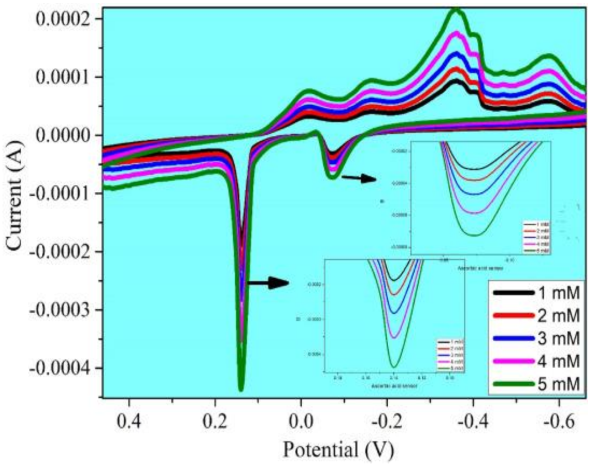
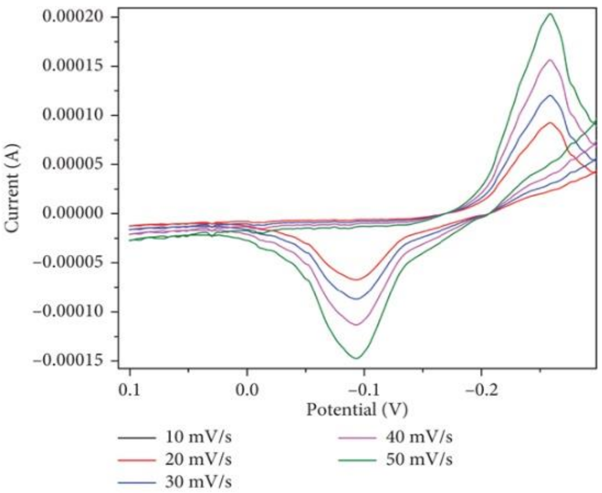


Fig. 8. Cyclic voltammogram of MoO_3 electrode

Fig. 9. Cyclic voltammogram of MoO_3 electrode for the detection of lead (concentration range 1-5 mM).

Synthesized using a straightforward and inexpensive probe sonication technique to produce bismuth oxide nanoparticles (Bi_2O_3 NPs). The synthesized nanoparticles showed high sensing ability for ascorbic acid and lead, suggesting its potential application in electrochemical sensing of biomolecules. CV studies done on the Bi2O3 electrode in 0.1 N HCl, revealing a specific capacitance value of 25.5.



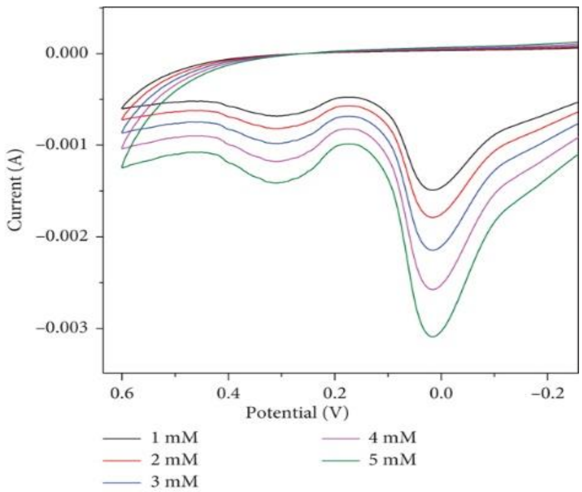


Fig.10. Ascorbic acid detection using the CV of Bi_2O_3 NPs

Fig. 11 CV of Bi_2O_3 NPs at varied scanning rates.

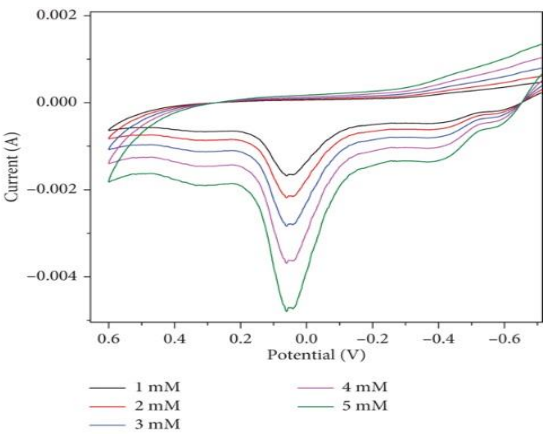


Fig. 12. CV of Bi_2O_3 NPs with detection of ascorbic acid lead

5. Conclusion:

The cyclic voltammetry (CV) technique is particularly valuable in nanoparticle sensor studies due to its effectiveness in providing real-time results. This method offers enhanced reliability, addressing the scientific challenge of accurately sensing specific metals or biomolecules in the presence of complex mixtures.

References:

1] Elgrishi, N., Rountree, K. J., McCarthy, B. D., Rountree, E. S., Eisenhart, T. T., & Dempsey, J. L. (2018). A practical beginner's guide to cyclic voltammetry. *Journal of chemical education*, *95*(2), 197-206.
https://pubs.acs.org/doi/10.1021/acs.jchemed.7b00361

2] Harini, H. V., Nagaswarupa, H. P., Bekele, E. T., Murthy, H. A., & Ravikumar, C. R. (2023). Novel synthesis of Cu2ZnAl2O4 nanostructures for photocatalytic and electrochemical sensor applications. *Sensors International*, *4*, 100225. https://doi.org/10.1016/j.sintl.2022.100225

3] Kumar, A. N., Jnaneshwara, D. M., Ravikumar, C. R., Murthy, H. C., Prashantha, S. C., Kumar, M. R., & Ajay, K. M. (2022). A Comparative Cyclic Voltametric Study on Rare Earth (Eu, Sm, Dy, and Tb) Ions Doped La 10 Si 6 O 27 Nanophosphors for Sensor Application. *Advances in Materials Science and Engineering*, *2022*.
https://doi.org/10.1155/2022/7429133

4] Rashmi, B. N., Harlapur, S. F., Gurushantha, K., Ravikumar, C. R., Kumar, M. A., Santosh, M. S., ... & Murthy, H. A. (2022). Facile green synthesis of lanthanum oxide nanoparticles using Centella asiatica and Tridax plants: photocatalytic, electrochemical sensor and antimicrobial studies. *Applied Surface Science Advances*, *7*, 100210. https://doi.org/10.1016/j.apsadv.2022.100210

5] Mamatha, K. M., Ravikumar, C. R., Murthy, H. A., Kumar, V. D., Kumar, A. N., & Jahagirdar, A. A. (2022). Facile green synthesis of Molybdenum oxide nanoparticles using Centella Asiatica plant: Its photocatalytic and electrochemical lead sensor applications. *Sensors International*, *3*, 100153.
https://doi.org/10.1016/j.sintl.2021.100153

6] Kusuma, K. B., Manju, M., Ravikumar, C. R., Dileepkumar, V. G., Kumar, A. N., Santosh, M. S., ... & Gurushantha, K. (2022). Probe sonicated synthesis of bismuth oxide (Bi2O3): photocatalytic application and electrochemical sensing of ascorbic acid and lead. *Journal of Nanomaterials*, *2022*, 1-13.
https://doi.org/10.1155/2022/3256611