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DEVELOPMENT OF TITANIUM DIOXIDE NANOPARTICLE-BASED ELECTROCHEMICAL SENSORS FOR LEAD AND CADMIUM DETECTION IN WATER SAMPLES

[1]Deepmala Dalal, [2]Dr. Neeraj Tomar
[1]Research Scholar, School of Sciences, Geeta University, Panipat (Haryana)
[2]Assistant Professor, School of Sciences, Geeta University, Panipat (Haryana)
[1]Email: deepmaladadalal@gmail.com

Abstract

The present study focuses on the successful development and characterization of a novel electrochemical sensor using a modified carbon paste electrode (CPE) integrated with titanium dioxide nanoparticles (TiO_2-NPs) for the detection of toxic metal ions in water samples. Titanium dioxide nanoparticles were meticulously characterized using Fourier-transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD) and UV-Visible spectroscopy to elucidate their structural and morphological properties. The TiO_2/CPE sensor was fabricated through a methodical process involving the homogeneous mixing of TiO_2 nanoparticles, graphite powder, and paraffin oil. Subsequently, this mixture was compacted into a Teflon tube with a copper wire serving as the electrical connector. Before utilization, the electrode surface underwent meticulous polishing and rinsing with double-distilled water to ensure optimal performance.

Keywords: Titanium dioxide nanoparticles, electrochemical sensor, water samples, toxic metal.

Introduction

Water contamination by heavy metals such as lead (Pb) and cadmium (Cd) poses a significant threat to environmental safety and public health [1-5]. These toxic elements, even at low concentrations, can have detrimental effects on human health, including kidney damage, bone fractures, and neurotoxic effects, especially in children. The primary sources of Pb and Cd in water systems [6-8] are industrial discharges, agricultural runoff, and improper disposal of electronic waste. Consequently, the development of sensitive and reliable methods for detecting these metals in water is of paramount importance.

Water pollution is a pressing issue in many parts of the world, including Panipat, Haryana. Panipat, known for its industrial activities, particularly in textile manufacturing, has been facing significant water pollution problems [9-13]. The discharge of untreated industrial effluents into water bodies has led to the contamination of local water sources with heavy metals, dyes, and other hazardous chemicals. This environmental degradation not only affects aquatic ecosystems but also poses serious health risks to the local population relying on these water sources for daily use. Though, there are various methods like, ion exchange, adsorption, photocatalytic degradation, sorption, oxidation processes for the treatment of waste waters [14-

20], but still there is a requirement of more specific and economically viable method.

Electrochemical sensing [21-25] has emerged as a promising approach for heavy metal detection due to its high sensitivity, selectivity, and rapid response. Among the various materials used in electrochemical sensors, metal oxides have garnered significant attention [26-32]. Titanium dioxide (TiO_2), commonly known as titania, is a metal oxide that stands out due to its excellent chemical stability, biocompatibility, and unique electronic properties [33-34]. Titania nanoparticles (TiO_2 NPs) offer a high surface area-to-volume ratio, enhancing their interaction with target analytes and improving sensor performance [35-38].

This research paper focuses on the development of titania nanoparticle-based electrochemical sensors for the detection of Pb and Cd in real water samples. The synthesis and characterization of TiO_2 NPs are critical steps in this process, ensuring that the nanoparticles exhibit the desired properties for effective sensing. The paper will detail the methods used for synthesizing TiO_2 NPs, their structural and morphological characterization, and their integration into electrochemical sensor platforms.

Furthermore, the study will evaluate the performance of these sensors in detecting Pb and Cd in various water samples, including tap water, river water, and wastewater. Key performance metrics such as sensitivity, selectivity, detection limits, and response times will be discussed. The potential interference from other common ions in water samples will also be examined to assess the robustness of the sensors.

By developing a reliable and efficient sensor for Pb and Cd detection, this research aims to contribute to environmental monitoring efforts and public health protection. The findings could pave the way for the broader application of TiO_2 NP-based sensors in environmental analysis and potentially in other fields such as food safety and biomedical diagnostics. This innovative approach to monitoring water quality is crucial for addressing the growing concerns of water pollution in industrial regions like Panipat and ensuring the safety and well-being of affected communities.

Experimental

Materials used

Titanium (IV) Chloride ($TiCl_4$) with a purity of 99.9%, ammonium hydroxide (NH_4OH, 30%), and glycerol (purity: 99.5%) were procured from Merck. All chemicals were of the highest purity grade and were used as received without further purification. For all experimental procedures,deionized water was utilized.

Instruments used

Fourier-transform Infrared Spectroscopy (FTIR), performed with a spectrometer equipped with a wide-range infrared source and detector for identifying chemical bonds and functional groups whereas Field Emission Scanning Electron Microscopy (FESEM), employing a high-resolution electron microscope to visualize nanoparticle morphology and structure at low voltages; and UV-Visible Spectroscopy, conducted with a spectrophotometer covering the UV and visible light spectra to analyze electronic transitions and optical properties. Electrochemical characterizations were performed using a Potentiostat/Galvanostat (AUTOLAB-PGSTAT 302 N, Metrohm). The electrochemical cell was configured with three electrodes: a modified carbon paste electrode as the working electrode, a platinum wire (Pt) as the counter electrode, and a reference electrode.

Synthesis of the nanoparticles

TiO_2 nanoparticles (NPs) were synthesized [33] using chemical precipitation method. First step includes the hydrolyzing $TiCl_4$ in a reaction medium with and without glycerol. For the same, 0.1Moles of 9.1117 M $TiCl_4$ was added drop-wise to a solution containing water and glycerol in a 1:1 ratio, maintained in an ice bath under vigorous stirring. On completion of the reaction, 300 mL of 2.5 M NH_4OH (serving as the precipitating agent) was added drop-wise to the solution until the pH reached 10. At this pH, white precipitates of TiO_2 appeared in the solution.Subsequently, the liquid phase was decanted from the solid phase, and the resulting precipitates were centrifuged at 4000 rpm for 10 minutes. The precipitate was washed several times to ensure the complete removal of Cl^- ions. All prepared samples were dried overnight in an oven at 80°C. The dried samples were then manually ground into a fine powder using a pestle and mortar. In some cases, the TiO_2 powder was calcined at 400°C for 1 hour at a heating rate of 10°C/min, resulting in a black powder.This heat treatment allowed the particles to achieve a more ordered and stable crystal structure, which is essential for their effective use in electrochemical sensors.

Characterization of nanoparticles

Titanium dioxide (TiO_2) nanoparticles have been characterized using a variety of analytical techniques. Fourier-transform infrared spectroscopy (FT-IR) was used to detect specific functional groups and analyze the chemical composition of the nanoparticles. Field emission scanning electron microscopy (FESEM) offered high-resolution images of the nanoparticle surfaces, allowing for detailed observation of their morphology and size. Additionally, UV-Visible spectroscopy was utilized to study the optical properties and electronic structure, helping to determine the absorption and bandgap characteristics of the nanoparticles.

Fabrication of electrochemical sensors from TiO_2 NPs

The process of creating the TiO_2-based electrode involved thoroughly mixing titanium dioxide nanoparticles (TiO_2NPs) with graphite powder and 250 µL of paraffin oil (Figure 1). This mixture was blended uniformly for 30 minutes using a mortar and pestle. After achieving a consistent paste, it was carefully packed and compressed into a Teflon tube with a diameter of 5 mm, which served as the electrode holder. A copper wire was used as the electrical connector to ensure proper conductivity.

Before the electrode could be used, its surface needed to be polished. This was done by gently rubbing the surface on smooth paper to achieve a refined finish. The electrode was then rinsed with double-distilled water to remove any residual particles and ensure a clean surface. This preparation step was crucial for ensuring the electrode's performance and accuracy during subsequent use.

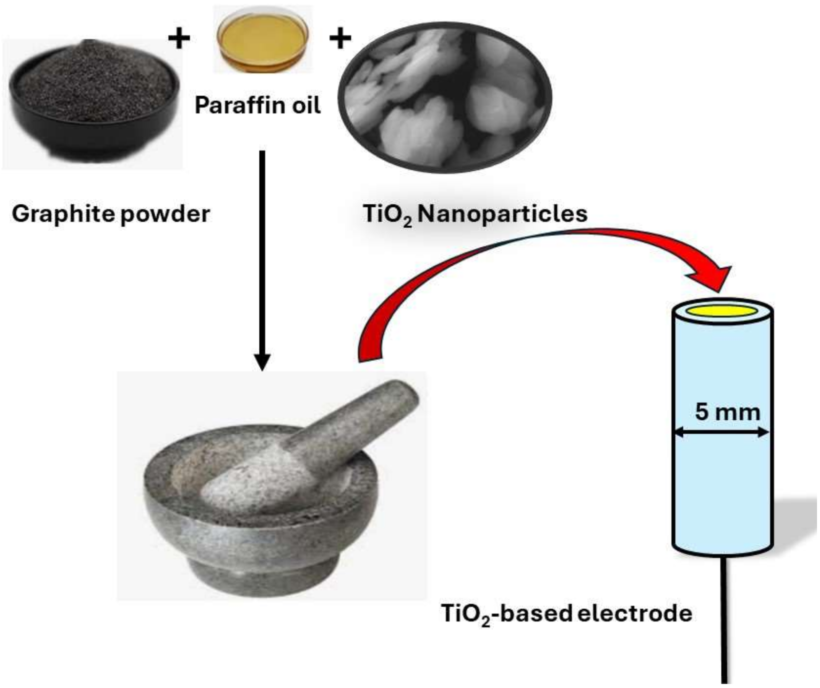


Figure 1: Schematic illustration of fabrication of TiO_2-based electrode

Electrochemical study

Differential Pulse Voltammetry (DPV) measurements were carried out in 0.1 M HNO_3, chosen as the optimal electrolyte, with a potential range of -0.1 to 0.4 V. All electrochemical responses were recorded at room temperature (25±2 °C).

Real water sample analysis

Water sampleswere collected from Dadlana and Nohra area situated at Haryana in the pre-cleaned water bottles. This sample was tested for lead and cadmium using the reported electrochemical sensor. Simultaneously, a portion of the same sample was sent to an outsourced agency for lead and cadmium testing. The results are presented in Table 1 and discussed in the results and discussion section.

Results and Discussion.

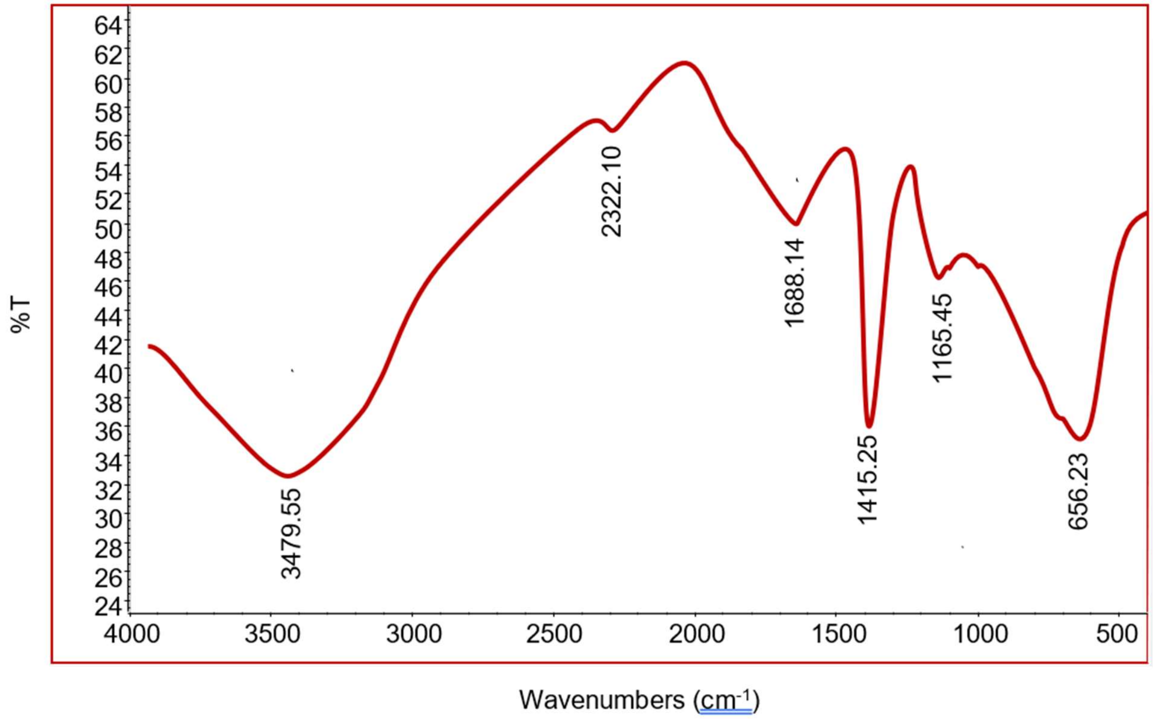
TiO_2 nanoparticles were synthesized using chemical precipitation method as explained in experimental section which has been characterized using Fourier Transform Infrared Spectroscopy (FTIR), as shown in Figure 2. The FTIR spectrum of TiO_2 nanoparticles reveals several characteristic peaks [39-40] that provide insights into the chemical bonds and functional groups present in the material. The peak at 656.23 cm-1 is typically attributed to the stretching vibrations of Ti-O bonds in the TiO_2 lattice. This strong indication confirms the presence of titanium dioxide nanoparticles.

The peak observed at 1165.45 cm-1 may correspond to the Ti-O-C or Ti-O-Ti stretching vibrations. These peaks can arise due to the presence of surface functional groups or organic residues from the synthesis process. Additionally, the peak at 1415.25 cm-1 is often associated with the bending vibrations of O-H groups, indicating the presence of hydroxyl groups on the surface of the TiO_2 nanoparticles.The peak at 1688.14 cm-1 suggests the presence of stretching vibrations of C=O bonds, which could be due to carbonyl groups from organic contaminants or residual solvents used during synthesis. Meanwhile, the peak at 2322.10 cm-1 could be associated with the stretching vibrations of adsorbed CO_2 or carbon-containing groups, sometimes observed due to atmospheric CO_2 being adsorbed onto the surface of the nanoparticles.

Finally, the broad peak at 3479.55 cm-1 is characteristic of O-H stretching vibrations, indicating the presence of hydroxyl groups or adsorbed water molecules on the surface of the TiO_2 nanoparticles. This is a common feature in FTIR spectra of nanoparticles exposed to the atmosphere.Thus, the FTIR spectrum confirms the presence of titanium dioxide and suggests that the nanoparticles have surface hydroxyl groups, possible organic residues, and adsorbed water or atmospheric gases. This information is crucial for understanding the surface chemistry and potential reactivity of the nanoparticles in various applications.

Figure 2: FTIR spectra of TiO_2 Nanoparticles

Scanning Electron Microscopy (SEM) analysis of TiO_2 nanoparticles conducted at an accelerating voltage of 25 kV reveals crucial information about the morphology and size of the nanoparticles. The high-energy electron beam provides detailed surface images, allowing for a thorough examination of the nanoparticle characteristics.The SEM image (Figure 3) typically shows well-dispersed TiO_2 nanoparticles with a fairly uniform size distribution around 10 nm. This small particle size suggests a high surface area, which is advantageous for various



applications such as catalysis, sensing, and photodegradation. The spherical or nearly spherical shape of the nanoparticles, as often observed in SEM images, indicates a well-controlled synthesis process that prevents agglomeration and ensures uniformity.The high resolution of SEM at 25 kV allows for the visualization of surface texture and porosity of the nanoparticles. Any agglomerates observed can indicate interactions between nanoparticles, but ideally, the images should show discrete, non-agglomerated particles. The detailed surface morphology provided by SEM can also reveal the presence of any surface defects or irregularities, which are crucial for understanding the reactivity and functional properties of the TiO_2 nanoparticles.

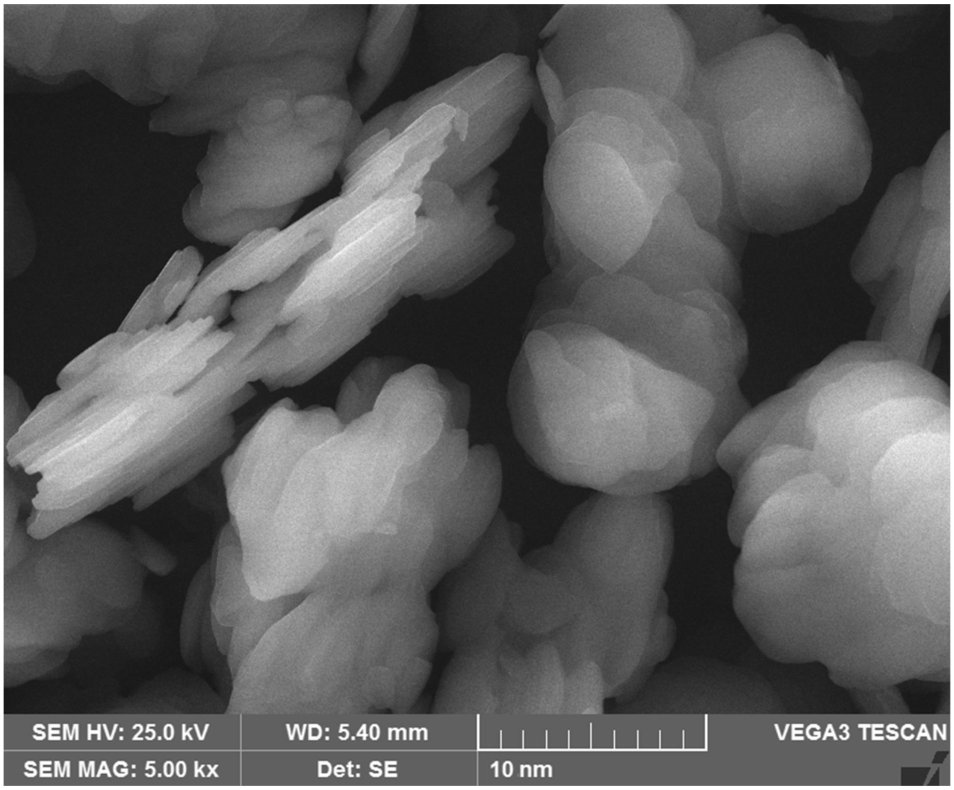


Figure 3: SEM image of TiO_2 Nanoparticles

The UV-Visible (UV-Vis) spectrum of TiO_2 nanoparticles (Figure 4) showing a single peak at 335 nm wavelength indicates a distinct absorption band, which is characteristic of the electronic transitions within the material. This peak corresponds to the bandgap energy of the TiO_2 nanoparticles, signifying the transition of electrons from the valence band to the conduction band. The specific wavelength at 335 nm suggests that the TiO_2 nanoparticles possess a relatively high energy bandgap, typical of nanoscale titanium dioxide. This sharp absorption peak reflects the purity and uniformity of the nanoparticles, as well as their potential efficacy in applications such as photocatalysis and UV filtration, where strong absorption in the UV range is crucial.

The XRD patterns of the synthesized nanoparticles provide insights into their semicrystalline nature. This is evidenced by the presence of several distinct peaks in the spectra, which suggest partial crystallinity within the material. These peaks, as depicted in Figure 5, reflect the ordered regions within the nanoparticles, while the absence of sharper peaks indicates the presence of amorphous or disordered phases. This combination of crystalline and amorphous regions is characteristic of semicrystalline materials.

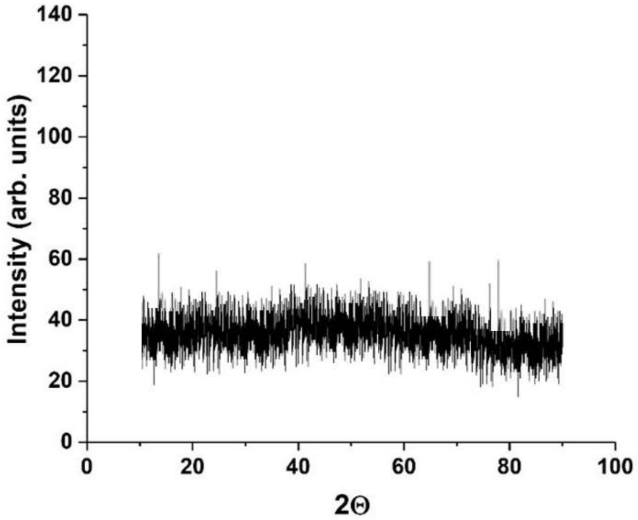


Figure 5: XRD spectra of TiO_2 Nanoparticles

The fabrication of the sensor has been successfully completed, and it is currently being tested for the detection of toxic metal ions in real-time water samples from Panipat, Haryana. This testing is particularly important due to the high industrial activity in Panipat, which is known for its textile and chemical industries. These industries can potentially lead to the contamination of local water sources with hazardous metal ions, posing significant health risks to the population. The development and testing of this sensor aim to address these environmental and public health concerns by providing a reliable method for monitoring water quality and ensuring the safety of the community.

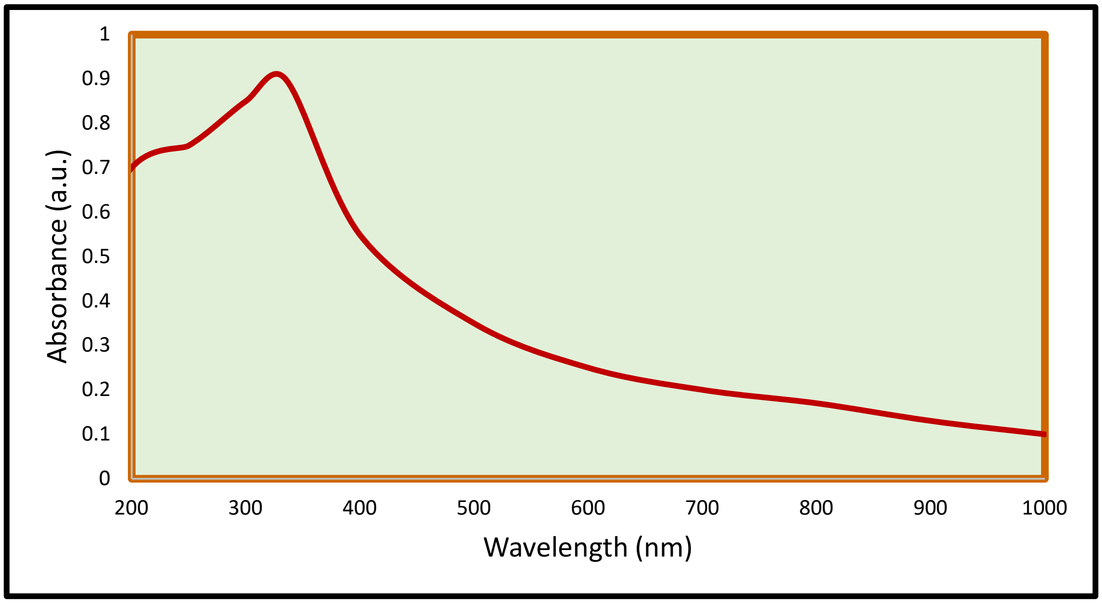
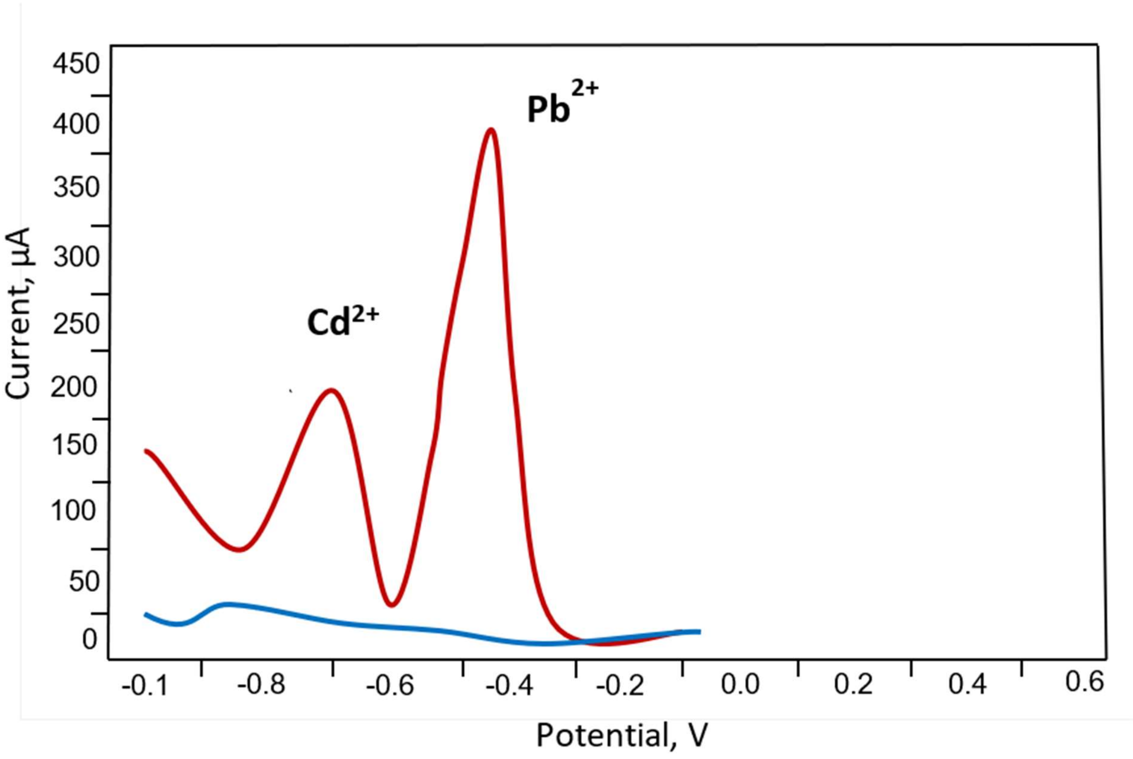


Figure 4: Uv-vis spectra of TiO_2 Nanoparticles

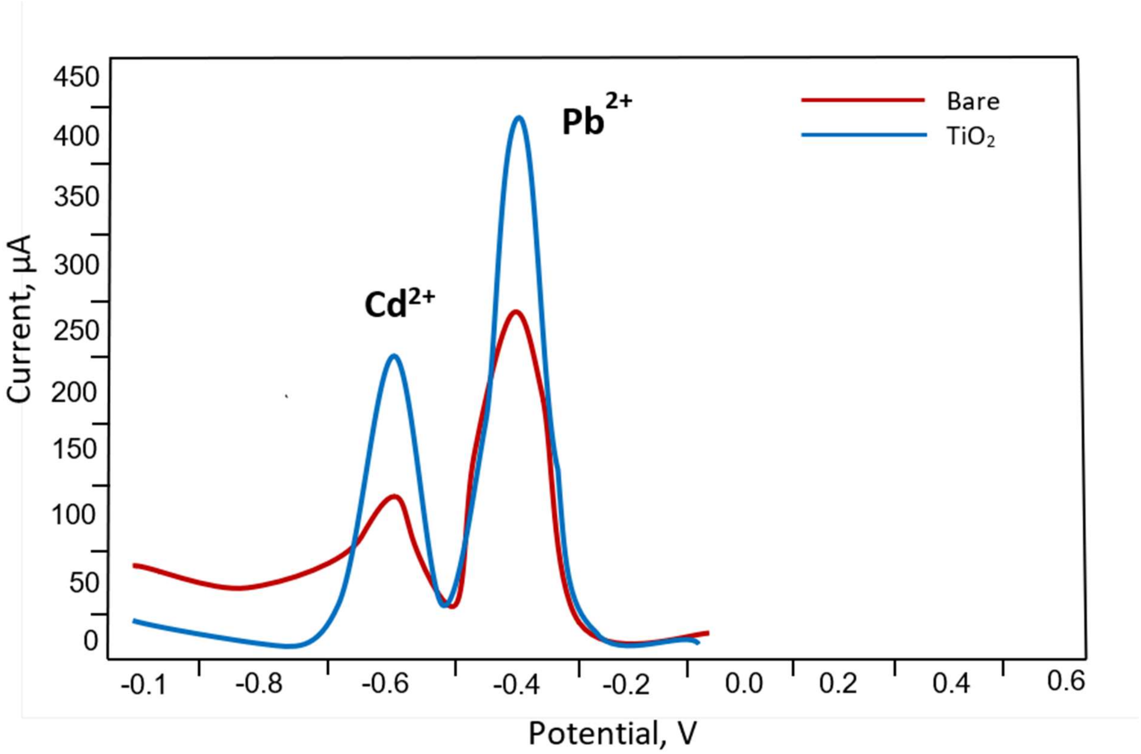
From the DPV measurements (Figure 6A), anodic peaks for Pb^{2+} and Cd^{2+}ions appeared at designated potentials of -0.4 V and -0.61 V respectively. Regarding the anodic peak heights, two distinct responses to the heavy metals were observed from the unmodified and TiO_2-modified electrodes. The modified surfaces exhibited an increase in peak height by several orders of magnitude, as shown in Figure 6B. This synergistic enhancement is attributed to the high electro-catalytic activity of TiO_2 nanoparticles (NPs) and the expanded electrode surface due to the addition of nanomaterial into its matrix.

As a proposed sensing mechanism, at the beginning of the electrochemical reaction [41], heavy metal ions in their cationic forms are adsorbed onto the electrode surface through electrostatic interaction with the negatively charged surface of the titania NPs. Subsequently, the adsorbed cationic metal ions are electrochemically reduced to their metallic form (M^o) under the applied voltammetric potential, which is then oxidized to generate the anodic peak currents.

$$M^{2+} + Ga_2O_3 \rightarrow M^{2+} - Ga_2O_3 \text{ ......adsorption}$$



(A)



(B)

Figure 6 (A): DPV responses of the TiO_2-based electrode, recorded in the plain supporting electrolyte (0.1 M HNO_3, represented by the blue line) and after injecting a mixture of the target metal ions (Pb^{2+} and Cd^{2+}) at a concentration of 0.001 M (represented by the red line), (B): The DPV signals of the TiO_2/CPE electrode, compared with the bare electrode in 0.1 M HNO_3 containing 0.001 M of Pb^{2+}, Cd^{2+}, and Hg^{2+} ions.

The practical evaluation of the modified electrodes was conducted using a real water samples from Panipat, Haryana. Before measurement, the samples were filtered to remove large particulates. The results obtained with the modified electrodes were compared to those from ICP-MS. As shown in Table 1, the concentration of Pb(II) in the samples was approximately 65 µM and 74µM for both samples with a relative error of 5.61% and 3.72%, respectively compared to the ICP-MS results whereas the Cd (II) was 44 µM and 45 µMwith a relative error of 3.98% and 11.22%, respectively as per ICP-MS results. Thus, the modified electrode demonstrated practical application potential.

Table 1: Comparison of TiO_2-modified electrodes and ICP-MS methods for determining Pb(II) and Cd(II) ions in a real water samples

Ions, to be detected	Detected by present report (µM)		ICP-MS (in µM by outsource method)		Relative error (%)	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
Lead (II)	61.35	71.25	65	74	5.61	3.72
Cadmium (II)	42.25	39.95	44	45	3.98	11.22

Conclusion

The successful fabrication and characterization of the TiO_2/CPE sensor for detecting toxic metal ions in water samples from Panipat, Haryana represent a significant advancement. The integration of titanium dioxide nanoparticles (TiO_2-NPs) into the carbon paste electrode (CPE) was confirmed through rigorous characterization using FTIR, FESEM, and UV-Visible spectroscopy, which elucidated the structural, morphological, and optical properties of the nanoparticles. The sensor's preparation involved precise mixing of TiO_2-NPs, graphite powder, and paraffin oil, followed by electrode packing and surface preparation.This study underscores the importance of such sensors in regions like Panipat, known for extensive industrial activity potentially impacting water quality. Further, the modified electrodes were effectively evaluated using a real water sample from Panipat, Haryana, demonstrating their practical application potential. The reported findings indicate their practical reliability and accuracy for heavy metal detection in environmental samples.

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