



Nano Cd (II) Schiff base complexes: Synthesis, characterization and its evaluation as a sensor for cadmium ions contamination at the low limit of detection by the QCM-based sensor method



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Abstract

Cadmium (Cd) contamination in water and soil is a significant environmental concern exacerbated by crop uptake and bioaccumulation of Cd. Monitoring Cd levels in the environment is crucial to minimize human exposure and associated health risks. In this context, we have developed a novel method for synthesizing cadmium complex nanoparticles, which offers an environmentally sustainable and reliable approach with potential applications in various fields. This research presents an advanced Nano cadmium complex sensor to detect cadmium ions. The Nano cadmium complex was comprehensively characterized using multiple analytical techniques, including Dynamic Light Scattering (DLS), Zeta potential analysis, Atomic Force Microscopy (AFM), Fourier-Transform Infrared (FT-IR) spectroscopy, contact angle measurements, BET surface area determination, and pore size analysis. We explored the potential of the Nano cadmium complex as a Quartz Crystal Microbalance (QCM) sensor, chosen for its simplicity, cost-effectiveness, and high sensitivity, focusing on rapid cadmium detection. The developed Nano cadmium complex based-QCM sensor demonstrates high selectivity and sensitivity, capable of detecting cadmium at concentrations as low as 0.1 ppm. We evaluated the sensor's performance in identifying cadmium ions under varying pH levels and temperatures. Additionally, we assessed the cytotoxic effects of the cadmium complex nanoparticles. This method effectively detects Cd [II] ions in groundwater and industrial effluent wastewater samples, serving as a valuable environmental monitoring and protection tool. The research contributes to developing sensitive and specific sensors for heavy metal detection, addressing the critical need for efficient environmental contaminant monitoring systems.

Keywords: Cadmium; Nanoparticles; QCM sensor; AFM; BET; Zeta potential

1. Introduction

Cadmium (Cd) contamination has emerged as one of the most pressing global environmental concerns due to the element's ubiquitous presence, high bioaccumulation potential, and profound toxicity [1-5]. This heavy metal exists in various forms within ecosystems, such as settled, soluble, adsorbed, or accumulated within living organisms. A comprehensive assessment of its bioavailability is required to accurately determine associated health risks [6-8]. The widespread industrial utilization of cadmium significantly contributes to its environmental dissemination. It finds applications in manufacturing batteries, alloys, pigments, coatings, and electroplating products. Moreover, cadmium is a common contaminant in phosphate fertilizers and sewage sludge used in agriculture [9]. Regrettably, the uncontrolled release of this hazardous substance poses significant dangers to both human health and ecological systems. From a human health perspective, cadmium exposure poses a serious risk. When inhaled or ingested, cadmium accumulates in vital organs such as the kidneys, liver, and bones [10, 11]. This process precipitates physiological disorders such as renal dysfunction, disturbances in calcium metabolism, osteoporosis, and an increased risk of certain cancers [12]. Cadmium's persistence in the environment and propensity for bioaccumulation through food chains have profound implications for ecological integrity. Aquatic organisms can accumulate significant concentrations, rendering them unsuitable for consumption. Additionally, cadmium's phytotoxicity can impede plant growth, disrupt nutrient uptake, and compromise crop yields, posing a threat to food security [13]. To address this issue, concerted efforts have been made to develop robust analytical techniques for monitoring and quantifying cadmium contamination. Traditional instrumental methods like atomic absorption spectroscopy (AAS) and inductively coupled plasma mass spectrometry (ICP-MS) have played pivotal roles [14, 15]. However, these approaches often require complex sample preparation, expensive instrumentation, and skilled personnel, making them less suitable for routine environmental monitoring and on-site analysis. In recent years, nanoparticle-based sensors have emerged as a promising alternative, offering a complementary toolkit to conventional analytical techniques. These innovative sensing platforms leverage the unique properties of nanomaterials to achieve remarkable sensitivity and selectivity in heavy metal detection [16, 17]. The

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Received date 05 July 2024; revised date 04 August 2024; accepted date 06 August 2024

DOI: 10.21608/EJCHEM.2024.301871.9953

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development of nanotechnology itself is rapidly advancing through the application of artificial intelligence, which is revolutionizing the design and synthesis of new materials[18]. Among these, the Quartz Crystal Microbalance (QCM) sensor exploiting nanoparticles has garnered significant attention due to its cost-effectiveness, selectivity, high sensitivity, rapid response time, and potential for miniaturization [16, 19-21]. QCM sensors operate on the principle of piezoelectric properties of quartz crystals. When an alternating electric field is applied, the crystal oscillates at a characteristic resonant frequency. Adsorption of target analyses onto the surface alters the mass, resulting in a measurable frequency shift. By functionalizing the crystal's surface with tailored nanoparticles or nanocomposites, the QCM sensor can be highly selective and sensitive toward specific heavy metal ions, including cadmium [20]. Despite these advances, there remains an urgent need for a prompt, reliable, and susceptible sensor specifically tailored for cadmium detection in various environmental matrices. Our ongoing research aims to develop a comprehensive analytical sensor platform capable of efficiently identifying and quantifying heavy metals, with a particular emphasis on cadmium ions. This entails designing, synthesizing, and optimizing a singular sensor system that can selectively detect and accurately quantify various heavy metal species while exhibiting heightened sensitivity toward cadmium. Our research efforts encompass the exploration of novel nano-materials, surface functionalization strategies, and signal transduction mechanisms. One promising approach involves synthesizing tailored nanoparticles or nanocomposites with high affinity for cadmium ions. These nanomaterials can possess specific functional groups, morphologies, or surface charges that facilitate selective binding and preconcentration of cadmium, thereby enhancing sensitivity and detection limits. Furthermore, we are investigating the potential of incorporating biomolecules, such as aptamers, peptides, or enzymes, onto the sensor surface. These bioreceptors can exhibit exquisite selectivity and strong binding affinities toward cadmium, enabling precise and sensitive detection. Additionally, integrating signal amplification strategies, like enzymatic catalysis or redox cycling, can further enhance the sensor's response, allowing for detecting trace levels of cadmium in complex samples. Another critical aspect involves developing sensor arrays and multimodal detection platforms[22]. By combining multiple sensing modalities, such as electrochemical, optical, or mass-based techniques, we aim to create a comprehensive analytical tool capable of providing complementary information on cadmium speciation, bioavailability, and toxicity. This approach enhances measurement reliability and accuracy while elucidating cadmium's behavior and fate in various environmental compartments. Realizing this objective would represent a significant stride toward mitigating the harmful effects of cadmium pollution, facilitating timely interventions, and safeguarding environmental and public health. By addressing this critical need, our research aims to contribute to global efforts in combating the threat posed by cadmium contamination, thereby promoting sustainable development and a safer planet. Moreover, a susceptible and selective cadmium sensor would have far-reaching applications beyond environmental monitoring. It could be employed in industrial process control, food safety, and biomedical diagnostics. Real-time monitoring of cadmium levels in wastewater streams or atmospheric emissions in industrial settings could aid regulatory compliance and minimize occupational exposures[23]. Within food safety, such a sensor could screen agricultural products, seafood, and drinking water for contamination, ensuring adherence to permissible limits and protecting consumer health. Furthermore, integrating cadmium sensors into wearable or implantable devices could revolutionize biomedical diagnostics and personalized medicine. By continuously monitoring cadmium levels in biological fluids, these sensors could facilitate early detection of cadmium poisoning, enabling timely intervention and treatment[24, 25]. Additionally, they could aid in elucidating cadmium's role in disease pathogenesis, paving the way for novel therapeutic strategies and preventive measures. For practical applications, overcoming challenges related to sensor stability, interference from complex matrices, and real-world validation is crucial. The potential rewards of developing a sensitive and selective cadmium sensor are significant, promising advancements in environmental stewardship, public health, and sustainable industrial practices. Our research aims to develop a novel cadmium Schiff base complex sensor for efficient cadmium ion detection in environmental samples. We focus on synthesizing and characterizing a cadmium Schiff base complex, evaluating its performance as a QCM-based sensor for low-level cadmium detection, and demonstrating its efficacy, sensitivity, and potential for real-world applications. This work contributes to the global effort to address cadmium contamination through innovative sensing technologies. By harnessing the properties of Schiff base complexes and the sensitivity of QCM technology, we strive to create a highly effective sensor for monitoring cadmium pollution, ultimately contributing to a safer environment. Our approach combines advanced coordination chemistry with practical environmental monitoring needs, aiming to bridge the gap between laboratory innovations and real-world solutions for cadmium detection and management.

2. Experimental part.

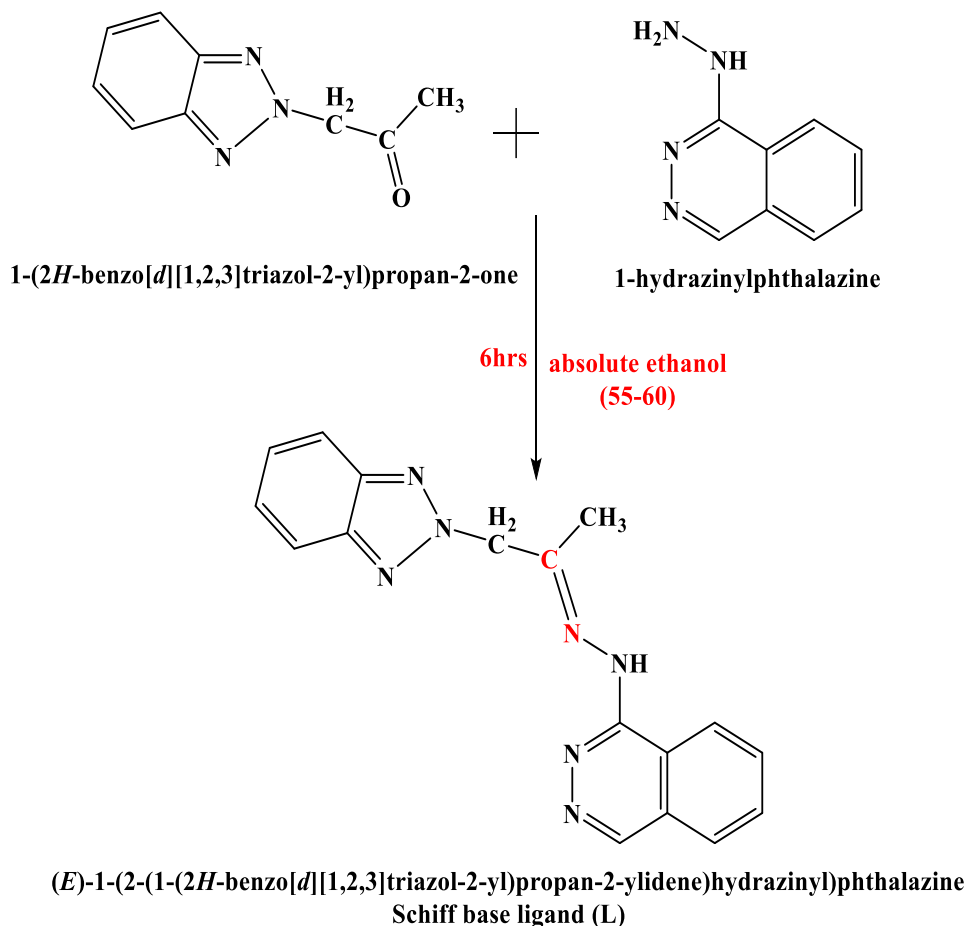
2.1. Experimental Procedures and Methodology.

2.1.1. Materials and Solutions

In this research study, high-purity chemicals were employed throughout the experimental procedures. The critical materials utilized included 1-hydrazinylphthalazine (obtained from Merck), 1-(2H-benzo[d][1,2,3]triazol-2-yl)propan-2-one (purchased from Sigma-Aldrich), and cobalt(II) chloride hexahydrate ($\text{CdCl}_2 \cdot 6\text{H}_2\text{O}$, sourced from BDH). For the preparation of solutions and as a reaction medium, absolute ethanol of spectroscopic grade purity was procured from BDH. Bidistilled water, obtained from glass distillation apparatuses, was consistently used for all aqueous solution preparations. It is important to note that all chemicals and reagents employed in this study were of high purity and used as received from the suppliers without further purification or treatment steps. Using high-quality materials and solvents is crucial in ensuring the reproducibility and accuracy of the experimental results and the successful synthesis and characterization of the desired compounds and nanostructures.

2.1.2. Synthesis of Schiff base ligand (L)

Continuing our previous work [26], the standard protocol synthesized a novel Schiff base ligand as in Reference [27]. The reaction was carried out by condensation of 1-hydrazinylphthalazine (1.24 mmol, 0.2 g), which was dissolved in hot absolute ethanol (55-60 °C), and 1-(2H-benzo[d][1,2,3]triazol-2-yl)propan-2-one (1.24 mmol, 0.218 g), which was dissolved in hot ethanol in a 1:1 molar ratio. The reaction mixture was then left under reflux for six h. Then, a reddish brown solid compound was separated after evaporation, and then the precipitate was filtered off and recrystallized from ethanol Solution to obtain a pure Schiff base with 88% yield. Scheme (1) presents the Schiff base ligand's general formation reaction mechanism and structure.



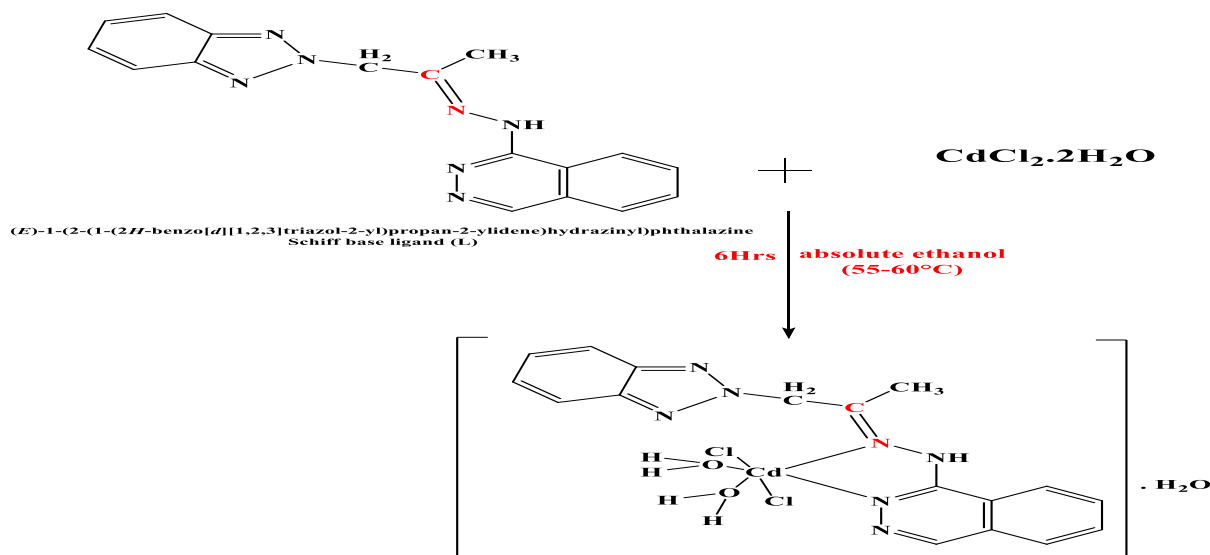
Scheme 1. Schiff base ligand (L)

2.1.3. Synthesis of Cadmium Complex and its Nanostructure

The fabrication of the Nano cadmium complex involved a sequential procedure. Initially, a heated ethanoic solution, maintained at (55-60°C), was prepared, incorporating the Schiff base ligand illustrated in Scheme 1 (0.94 mmol, 0.3 g).

In a distinct solution of absolute ethanol (20 ml) heated separately, the metal salt (0.94 mmol, 0.19 g CdCl₂) was dissolved. Following Five hours of consistent stirring under reflux conditions, the resultant complex commenced precipitation from the solution. Following precipitation, the consequent solids were gathered through filtration, underwent meticulous washing, and were ultimately desiccated under vacuum using anhydrous calcium chloride[23, 26, 27]. The purification phase was finalized through a recrystallization process.

An intriguing transformation occurred during this procedure, as the Colour shifted from reddish brown to dark brown (Scheme 2). Furthermore, the synthesized complex underwent ultrasonic probe treatment for 10 minutes[20, 28].



Scheme 2. visually illustrates the structure of the Cadmium Schiff base Complex and its formation reaction.

2.2. Instrumentation

This investigation, conducted at Cairo University in Egypt, employed a multifaceted analytical approach to characterize various materials comprehensively. The research involved diverse scientific instruments and methods to gain insights into the composition and characteristics of the studied materials. A range of techniques were utilized for material characterization. The microanalysis was conducted using a CHNS-932 (LECO) Vario Elemental analyzer at Cairo University's Microanalytical Center, explicitly targeting the determination of carbon, hydrogen, and nitrogen content in the samples. The materials' melting point was determined by employing a trforce XMTD-3000 apparatus [29]. Spectroscopic analyses included Fourier transform infrared (FT-IR) spectra obtained using a Perkin-Elmer 1650 spectrometer with KBr disks, covering a spectral range from 4000 to 400 cm^{-1} [27]. Mass spectra were acquired using an MS-5988 GS-MS instrument manufactured by Hewlett-Packard, which employed the electron ionization method at 70 eV [30]. UV-Vis spectra of solutions within the 200 to 700 nm wavelength range were recorded using a UV-Vis PerkinElmer Model spectrophotometer. To gauge the molar conductance of solid complex solutions in ethanol at a concentration of 10^{-3} M, a Jenway 4010 conductivity meter was utilized [31, 32]. Surface and particle characterization techniques were also employed. The surface charge and particle size were determined using a NanoSight NS500 instrument from Malvern Panalytical to characterize the nano cadmium complex. The BET surface area and pore volume were ascertained utilizing a surface area and pore volume analyzer (Quanta Chrome, Nova Touch 4L, USA) employing multi-point and DH pore volume methods [33]. Before analysis, the metal complex nanoparticles underwent degassing at 65°C for 1.25 hours to ensure accurate measurements. AFM investigations were conducted employing an Oxford-manufactured AFM instrument, specifically the Jupiter XR AFM model, to analyze the morphology of Cadmium complex nanoparticles [34]. In preparation for AFM analysis, the samples underwent a 10-minute sonication process using an ultrasonic probe sonicator (UP400S, Hielscher, Oderstraße, Teltow, Germany) at a frequency of 55 kHz, an amplitude of 55%, and a cycle of 0.55. The AFM images and roughness profiles were obtained at 47 nm x 47 nm, employing a gold tap, contact mode, and a scanning speed of 0.31 In/S. For sensor fabrication and thin film synthesis, a Spain coater instrument (Laurell-650Sz, France) was used under vacuum conditions, with a rotational speed of 750 rpm and a rate of 50 μm per 120 seconds. The thin film was created using this apparatus under vacuum conditions, employing a rotational speed of 750 revolutions per minute (rpm) and a deposition rate of 50 μm every 120 seconds. A Biolin Scientific contact angle analyzer (model T200) was utilized to assess wettability, operating under sessile drop conditions [35]. The measurements were conducted with a 10-second duration and a droplet volume of 4 μL of distilled water. Sensor testing involved the use of an AT-cut quartz crystal chip to establish QCM-based cadmium complex nanosensors affixed to a gold electrode with a 12 mm diameter and a resonance frequency of 5 MHz (Q-Sense, Shenzhen, China) [35]. The sensor preparation process included a cleaning step involving immersion in a solution of aqueous ammonia, H_2O_2 , and double-distilled water (5:1:1 v/v/v) for 10 minutes at 75°C. Subsequently, the sensor was rinsed with double-distilled water and ethanol before being air-dried at room temperature. The dried chip was then inserted into the Q-Sense instrument. The QCM measurements were initiated by introducing a background electrolyte solution (consisting of double-distilled water into the QCM module to initiate baseline measurements before incorporating the sensor's nano-materials. To maintain a stable QCM signal, continuous infusion of double-distilled water was carried out until the QCM signal reached a recorded value of zero. Subsequently, 2 mL of a (0.1, 0.5, and 1) ppm cadmium complex NP solution was mixed with 10 mL of double-distilled water. Following this preparation, a portion of the mixture was introduced onto the gold sensor at a controlled flow rate of 0.4 mL/min [19, 20]. Biological testing encompassed antimicrobial research conducted at the Microanalytical Center at Cairo University, while cytotoxicity studies were executed at the National Cancer Institute and

Cairo University [36, 37]. This comprehensive analytical approach allowed for a detailed examination of the surface characteristics and morphology of the Cadmium complex nanoparticles, providing valuable insights into their structural features and potential applications as sensors for cadmium detection.

2.3. QCM-Monitoring of cadmium ions.

The Quartz Crystal Microbalance (QCM) assessments employed a QCM system from Qsenses, Biolin Scientific, located in Linthicum Heights, MD, USA [38–40] (Fig 1). Each Quartz Crystal Microbalance (QCM) measurement involved introducing 1 ppm cadmium solutions onto the surface of QCM-based nanosensors designed for cadmium complex detection. These measurements were conducted across varying concentrations (1, 0.5, 0.1 ppm), diverse temperatures (25°C, 35°C, and 45°C)[41], and different pH levels (4, 7, and 10). The injection of the cadmium solution was iteratively performed until the signal reached a stable state, indicating the attainment of equilibrium in the binding interaction between the nanosensors and cadmium ions. After a predetermined duration, double-distilled water was introduced into the module to eliminate unadsorbed particles from the QCM sensor surfaces. This process ensured the removal of any residual cadmium particles and facilitated the preparation of the Nanosensors for subsequent measurements [42–43].

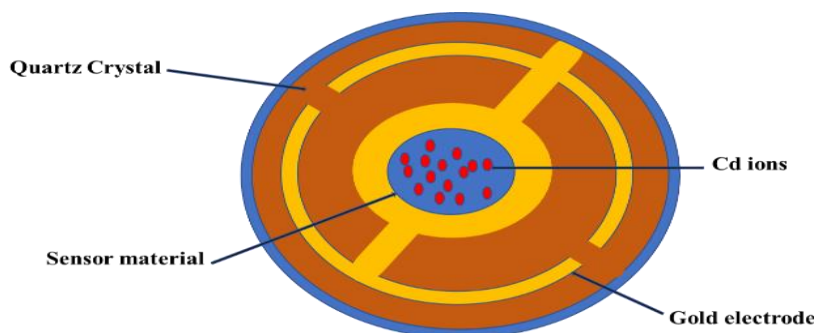


Fig 1. Experimental Setup for QCM Assessment of Cadmium Detection Using Qsenses QCM System.

3. Result and Discussion

3.1. Chemical composition and biological properties of Schiff base Cadmium complex

The cadmium complex stands out due to its distinct chemical composition and noteworthy biological attributes. This complex exhibit stability in air and readily dissolves in polar organic solvents such as ethanol (EtOH), methanol (MeOH), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). However, it demonstrates limited solubility in water. Elemental analysis affirms a 1:1 metal-to-ligand ratio for the complex. In DMF (concentration of 10^{-3} M) at 25 °C, its molar conductivity (Λ_m) registers at $35 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$, indicating its non-electrolytic nature[44, 45]. The newly synthesized Schiff base cadmium complex exhibited favorable characteristics with a yield of 78%, a melting point of 237°C, and presented as a dark brown solid. Elemental analysis results were in agreement with the calculated values for $[\text{Cd}(\text{L})(\text{H}_2\text{O})_2\text{Cl}_2] \cdot \text{H}_2\text{O}$ with the molecular formula ($\text{C}_{17}\text{H}_{21}\text{CdCl}_2\text{N}_7\text{O}_3$), confirming a 1:1 metal-to-ligand ratio and validating the composition of the complex[26, 27]. The EI-MS technique was used in this work to corroborate the mass of the cadmium complex by examining the intense molecular ion peaks in the spectra shown at $m/z = 555.40 [\text{M}^+]^+$. The coordination mechanism between the ligand and the cadmium center is revealed through a comparative analysis of the infrared spectra of the ligand and the cadmium complex. Notably, the azomethine group and N-phthalazine in the ligand exhibit a robust band at 1629 and 1584 cm^{-1} , respectively, which shift to 1619 and 1565 cm^{-1} in the complex [46, 47]. This shift signifies coordination through the two nitrogen atoms. Additional nonligand bands at 456 cm^{-1} and 582 cm^{-1} correspond to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ coordinated water, respectively [26–29], [48]. The triazole did not bind to the Cobalt metal cation, as shown by the unchanged band of the $\nu(\text{N}-\text{N})$ mode at 1088 cm^{-1} in the IR spectra of the Cobalt complex[49], [50]. Based on this data, the proposed formula for the cadmium complex is $[\text{Cd}(\text{L})(\text{H}_2\text{O})_2\text{Cl}_2] \cdot \text{H}_2\text{O}$. The UV-Vis spectrum of the cadmium complex reveals distinctive bands at 253 nm and 342 nm, indicative of $\pi-\pi^*$ and $n-\pi^*$ intramolecular transitions, respectively. Regarding biological activity, the antibacterial and antifungal properties of the cadmium complex were evaluated using the disc diffusion method[51–52]. Table 1 presents the antimicrobial activity, expressed as the zone of inhibition (in mm), of the free Schiff base ligand (L) and its corresponding Cd(II) complex against various gram-negative bacteria, gram-positive bacteria, and fungi (Table 1)[29], [53], [54]. While our focus is on cadmium detection, the successful use of functionalized iron oxide nanoparticles for malaria vaccine delivery demonstrates the versatility of nanoparticles in diverse biomedical applications[55]. The activity is compared with standard antibiotics such as gentamicin (for gram-negative bacteria), ampicillin (for gram-positive bacteria), and nystatin (for fungi). Against the gram-negative bacteria *Escherichia coli* (ATCC:10536) and *Salmonella enterica* (ATCC: 14028), the Cd(II) complex exhibits significantly higher antimicrobial activity than the free Schiff base ligand, with zones of inhibition of 26 ± 0.3 mm and 22.7 ± 1.0 mm, respectively. These values are comparable to or even higher than the standard antibiotic gentamicin, suggesting the potential of the Cd(II) complex as an effective antimicrobial agent against gram-negative bacteria. For the gram-positive bacteria *Staphylococcus aureus* (ATCC:13565) and *Streptococcus mutans* (ATCC:25175), the Cd(II) complex again demonstrates superior antimicrobial activity compared to the free ligand, with zones of inhibition of 18.7 ± 1.0 mm and 21 ± 0.3 mm, respectively. While the activity against *Staphylococcus aureus* is slightly lower than the standard

ampicillin, the activity against *Streptococcus mutans* is comparable to the standard. In the case of the fungi *Candida albicans* (ATCC:10231) and *Aspergillus Nigar* (ATCC:16404), the Cd(II) complex exhibits moderate to good antimicrobial activity, with zones of inhibition of 19 ± 0.6 mm and 27.2 ± 0.6 mm, respectively. Against *Aspergillus Nigar*, the Cd(II) complex outperforms the standard antifungal agent nystatin, highlighting its potential as an effective antifungal agent. Overall, the data suggests that the complexation of the Schiff base ligand with Cd(II) enhances its antimicrobial activity across a wide range of microorganisms, including gram-negative and gram-positive bacteria and fungi. The Cd(II) complex demonstrates promising antimicrobial potential, sometimes surpassing standard antibiotics' activity [26-27]. These findings are consistent with previous research on chitosan nanoparticles, which also demonstrated antibacterial activity [56].

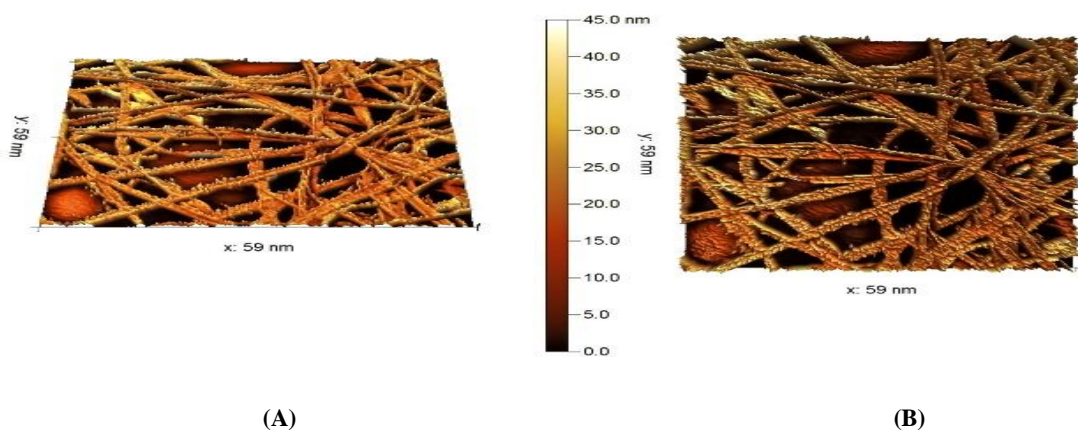
Table 1. Antimicrobial Activity (Zone of Inhibition in mm) of Schiff Base Ligand (L), Cd(II) Complex, and Standard Antibiotics against Various Microorganisms

Sample	Schiff base Ligand (L)	Cd(II) Complex	Standard antibiotic
Microorganism			
Gram-negative bacteria			Gentamicin
<i>Escherichia coli</i> (ATCC:10536)	10.3±0.6	26±0.3	27.0±1.0
<i>Salmonella enterica</i> (ATCC: 14028)	9.0±1.0	22.7±1.0	18.3±0.6
Gram-positive bacteria			Ampicillin
<i>Staphylococcus aureus</i> (ATCC:13565)	10.0±1.0	18.7±1.0	22.0±1.0
<i>Streptococcus mutans</i> (ATCC:25175)	15.3±0.6	21±0.3	20.3±0.6
Fungi			Nystatin
<i>Candida albicans</i> (ATCC:10231)	16.7±0.6	19±0.6	21.0±1.0
<i>Aspergillus Nigar</i> (ATCC:16404)	20.3±0.6	27.2±0.6	19.3±0.6

3.2. Characterization of Nano cadmium complex.

3.2.1. Textural characters (AFM) of cadmium complex Nanoparticles.

An atomic force microscope (AFM) was used to conduct a detailed analysis of the newly synthesized nano cadmium complex's surface morphology [57]. The AFM images vividly depicted a fibrous morphology, as illustrated in Figure 2. These images revealed no observable signs of aggregation or agglomeration [58]. The particle size, extrapolated from the AFM images, was established to be less than 59 nm.



(B) **Fig 2.**(A) Depict the 3D Atomic Force Microscopy (AFM) on the left, and (B) Depict the 3D Two-Dimensional Atomic Force Microscopy (2DAFM) on the right for Cd (II) complex nanoparticles.

3.2.2. DLS and Zeta Potential

The nano cadmium complex particle size assessment was conducted using the Dynamic Light Scattering (DLS) technique[59], as depicted in Figure 3. The analysis revealed that the average particle size of the nano cadmium complex was 51 nm. These results underscored a unimodal size distribution with a low polydispersity index, indicating a remarkably high colloidal stability within the suspension. Figure 4 illustrates the particle size distribution and Zeta potential outcomes for the nano cadmium complex. Notably, the measured Zeta potential was -15 mV, suggesting a uniform dispersion of nanoparticles. The Zeta potential, critical in evaluating physicochemical stability during storage, reflects the system's overall stability[60]. Notably, a higher absolute Zeta potential value corresponds to system stability. The outcomes presented here unequivocally highlight the nano cadmium complex's exceptional stability.

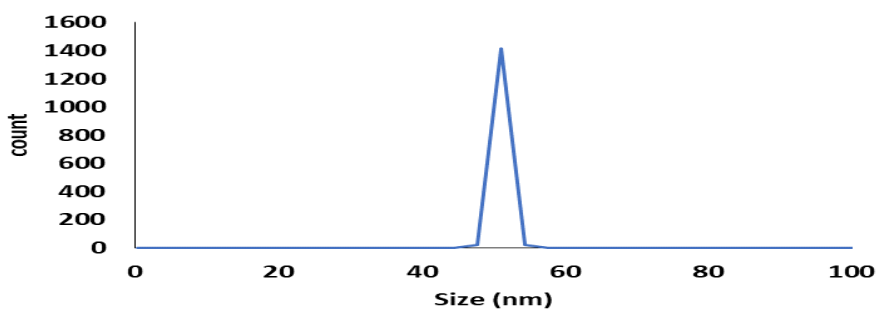


Fig 3. Particle Size Distribution Analysis of Nano Cadmium Complex.



Figure 4. Zeta Potential Analysis Confirms Enhanced Stability of Nano Cadmium Complex (-15 mV).

3.2.3. BET surface area and pore size

The BET (Brunauer–Emmett–Teller) methodology is a powerful tool for characterizing nanomaterials, providing valuable insights into their surface area and porosity. In the case of the nano cadmium complex specimen, applying BET adsorption isotherms played a crucial role in scrutinizing its surface area characteristics (Fig 5) [61-62]. The nitrogen adsorption-desorption isotherms exhibited a characteristic type IV behavior, indicating the presence of hysteresis loops, confirming the macroporous nature of these nanoparticles. The multipoint BET surface area analysis revealed an impressive value of 89.9257 m²/g, accompanied by an average pore size of 9.44856 nm and an average particle radius of 1.5164e+001 nm (approximately 15 nm). The substantial surface area, as elucidated by the multipoint BET analysis, significantly enhances the capacity of these metal complex nanoparticles to adsorb cadmium ions from aqueous environments. This remarkable surface area is attributed to the unique fibrous morphology of the nanoparticles, as evidenced by the AFM analysis, which reveals a fiber-like structure with a diameter of approximately 59 nm. The macroporous structural characteristics, stemming from the fibrous morphology, play a pivotal role in augmenting the efficacy of cadmium ion adsorption by these metal complex nanoparticles. The high surface area and macroporous nature provide abundant active sites and enhanced accessibility for cadmium ions to interact with the nanoparticle surface[63]. Furthermore, the fibrous morphology with a diameter of 59 nm contributes to the high surface area. It facilitates the adsorption process by providing a more significant number of binding sites and potential ion exchange channels along the length of the fibers. This unique fibrous architecture creates a highly conducive environment for efficient cadmium ion adsorption and subsequent removal from aqueous solutions[64], [65]. The macroporous structure, substantial surface area, and fibrous morphology with a favorable fiber diameter make these complex metal nanoparticles highly attractive for cadmium ion adsorption and remediation applications.

The synergistic effect of these characteristics enhances the nanoparticles' adsorption capacity, selectivity, and kinetics, ultimately leading to improved cadmium ion removal efficacy.

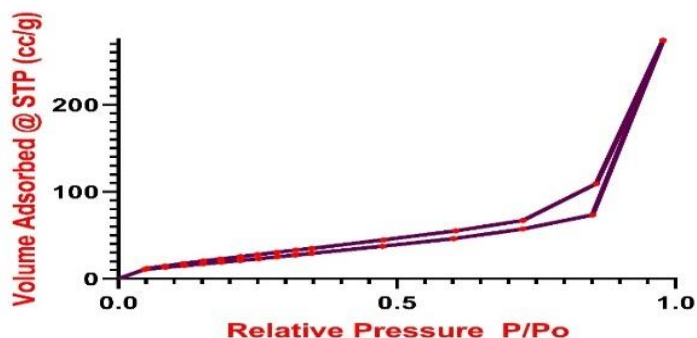


Fig 5. illustrates N₂-isotherm of Nano Cd (II) complex.

3.2.4. Contact angle, Hydrophobicity, and toxicity of cadmium Nano complex.

The hydrophobic nature of the nano cadmium complex particles is evident in the considerable water contact angle, measuring 109.7° (Fig 6). This inherent hydrophobic characteristic enhances the suitability of these nanoparticles for practical sensing applications in aqueous environments [66-68]. In the development of eco-friendly nanoparticle-based sensors, it becomes essential to guarantee the material's non-toxicity. A thorough evaluation of the cytotoxicity of the Nano cadmium complex resulted in a reassuring IC₅₀ value of 523 µg/ml [23, 69]. The notably high IC₅₀ value provides confidence in the potential utilization of the Nano cadmium complex as a sensor in water-related applications, emphasizing its safety and environmental compatibility.

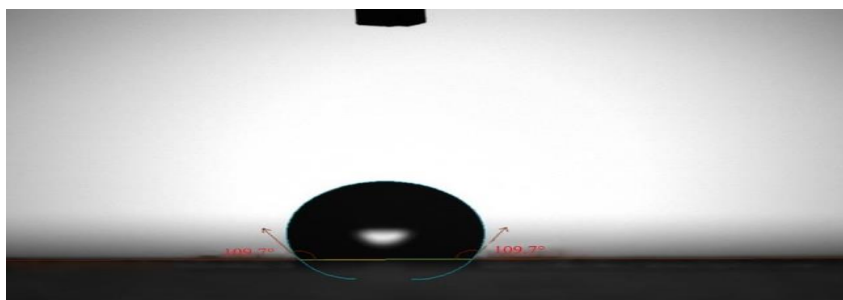


Fig 6. Hydrophobic Properties of Nano Cadmium Complex for Water Sensing Applications

3.2.5. QCM-Based Nanosensors for Cadmium Ion Detection: A Four-Phase Approach

Quartz Crystal Microbalance (QCM)-based nanosensors have emerged as a promising technique for detecting and monitoring cadmium ions in various environments. The sensing mechanism involves the immobilization of a cadmium-selective nanomaterial on the surface of a quartz crystal resonator. The detection process can be delineated into four distinct phases, each providing valuable insights into the sensor's performance and efficiency [19, 21, 23].

A) Phase I: Baseline Frequency Stabilization

Initially, the QCM sensor is exposed to the medium of interest, and the quartz crystal's resonant frequency is monitored until a stable baseline is established. This step ensures that the subsequent frequency changes can be attributed solely to the interaction between the cadmium ions and the nanosensor's surface.

B) Phase II: Rapid Frequency Reduction due to Cadmium Ion Binding

A rapid and substantial decrease in the resonant frequency is observed upon introducing cadmium ions into the medium. This abrupt change is attributed to the mass loading effect, wherein the cadmium ions bind to the available binding sites on the nanosensor's surface, causing an increase in the overall mass of the quartz crystal resonator. The magnitude of the frequency shift is directly proportional to the concentration of cadmium ions present in the medium.

C) Phase III: Continuous Adsorption of Cadmium Ions

As the exposure time increases, the adsorption of cadmium ions onto the nanosensor's surface continues, leading to a gradual decrease in the resonant frequency. This phase highlights the sensor's ability to capture additional cadmium ions,

potentially reaching saturation levels depending on the concentration of cadmium ions and the availability of binding sites on the nanosensor.

D) Phase IV: Equilibrium State in Adsorption

Eventually, an equilibrium state is reached, where the resonant frequency stabilizes, indicating that the nanosensor has reached its maximum adsorption capacity for cadmium ions under the given experimental conditions. At this stage, no significant changes in frequency are observed, suggesting minimal mass loss or structural alterations on the nanosensor's surface. The QCM-based nanosensor's performance is evaluated by monitoring the frequency shifts across these four phases. The sensor's sensitivity, selectivity, and detection limits can be determined by analyzing the frequency response patterns and correlating them with the known concentrations of cadmium ions in the test medium. Additionally, the nanosensor's surface can be functionalized with various cadmium-selective materials, such as chalcogenide nanostructures, metal-organic frameworks, or biopolymers, to enhance its specificity and sensitivity towards cadmium ions. These functionalized nanosensors can be tailored to suit different application domains, including environmental monitoring, industrial waste management, and biomedical diagnostics.

3.2.6. Proposed Sensing Mechanism of the QCM-Based Nano Cadmium Complex: A Synergistic Interplay of Interactions

The sensing mechanism of the QCM-based nano cadmium complex involves a synergistic interplay of various intermolecular interactions between the nanosensor and the cadmium ions[70]. The relative electronegativity differences between the cadmium ions and the nanosensor and the presence of specific functional groups and structural features within the nano cadmium complex govern the proposed sensing mechanism. Initially, dipole-dipole interactions may arise due to the relatively lower electronegativity of cadmium ions compared to the nanosensor. These dipole-dipole interactions can contribute to cadmium ions' initial recognition and binding to the nanosensor's surface. Additionally, π - π interactions between the aromatic or conjugated systems present in the nano cadmium complex and the polarizable cadmium ions may also enhance the binding affinity. The nano cadmium complex is often designed with polar side chains or functional groups that act as electron-donating moieties. These electron-donating groups contribute to an increased negative charge density on the nanosensor's surface, facilitating electrostatic interactions with the positively charged cadmium ions. The electrostatic and π - π interactions play a crucial role in the selective detection and strong binding of cadmium ions to the QCM-based nanosensor[23, 71-72]. The concentration of cadmium ions in the medium also influences the sensing mechanism. At lower concentrations, the initial binding of cadmium ions to the nanosensor's surface may be dominated by dipole-dipole and π - π interactions. As the concentration of cadmium ions increases, the electrostatic interactions become more prevalent, leading to a more potent and specific binding of cadmium ions to the nanosensor's surface. Furthermore, the nano cadmium complex may possess specific molecular recognition sites or chelating groups tailored for cadmium ion binding. These recognition sites can contribute to the selective binding of cadmium ions over other interfering ions, enhancing the sensor's specificity and sensitivity. The synergistic interplay of these intermolecular interactions, coupled with the tailored molecular design of the nano cadmium complex, enables the QCM-based nanosensor to selectively detect and quantify cadmium ions in various matrices, making it a promising analytical tool for environmental monitoring, industrial applications, and biomedical diagnostics.

3.2.7. Effect of concentration

The sensitivity of the Schiff base nano cadmium complex towards cadmium ions is influenced by the concentration of the cadmium solution, as depicted in Figure 7. The figure illustrates the response of the QCM-based sensor employing the Schiff base nano cadmium complex to different concentrations of cadmium ions, ranging from 0.1 ppm to 1 ppm[73-74]. All three concentrations exhibit a similar pattern of resonance frequency changes (Δf), characterized by a rapid decrease in frequency within 3 minutes of exposure to the cadmium solution. Notably, the magnitude of the frequency shift (Δf) is directly proportional to the concentration of cadmium ions present in the solution. As the concentration increases from 0.1 ppm to 0.5 ppm and subsequently to 1 ppm, a more significant frequency shift is observed, indicating a higher mass loading on the QCM sensor surface due to the increased adsorption of cadmium ions. This behavior suggests that the Schiff base nano cadmium complex possesses a higher sensitivity towards higher concentrations of cadmium ions, enabling more efficient detection and quantification[20,23] [73-74]. Furthermore, the rapid response time observed across all concentrations, with frequency modulation occurring within the first 3 minutes, highlights the exceptional kinetics of the Schiff base nano cadmium complex towards cadmium ion binding. This rapid response time is advantageous for real-time monitoring and detection applications, ensuring prompt identification of cadmium ion contamination in various matrices. The ability of the Schiff base nano cadmium complex to differentiate and respond to varying concentrations of cadmium ions demonstrates its potential for quantitative analysis and concentration-dependent sensing. This concentration-dependent behavior, coupled with the rapid response time, underscores the suitability of the QCM-based sensor employing the Schiff base nano cadmium complex for sensitive and reliable detection of cadmium ions in environmental, industrial, and biomedical settings.

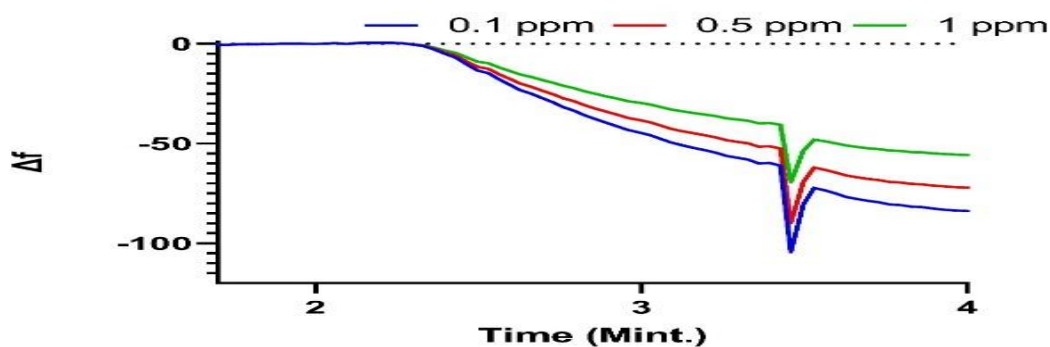


Fig 7. QCM Response of Schiff Base Nano Cadmium Complex to Different Cadmium Ion Concentrations

3.2.8. Effect of temperature

Figure 8 illustrates the influence of temperature on the QCM-based sensor's response to cadmium ion detection. Three different temperatures, 25°C, 35°C, and 45°C, were evaluated to assess the effect of temperature on the sensor's performance (Fig 8). The graph depicts the changes in resonance frequency (Δf) over time for the Schiff base nano cadmium complex at these different temperatures [75]. At the lower temperature of 25°C, the frequency shift (Δf) exhibits a relatively gradual decrease, indicating a slower kinetic response of the Schiff base nano cadmium complex towards cadmium ion binding. This behavior suggests that the intermolecular interactions responsible for the binding process, such as electrostatic, π - π , and dipole-dipole interactions, may be less favored at lower temperatures, leading to a reduced rate of cadmium ion adsorption on the sensor surface [76, 77]. As the temperature increases to 35°C, a more pronounced and rapid decrease in the resonance frequency is observed, implying a faster kinetic response and enhanced binding of cadmium ions to the Schiff base nano cadmium complex. This performance improvement can be attributed to the increased thermal energy, which facilitates the forming and strengthening the intermolecular interactions between the nano cadmium complex and the cadmium ions, resulting in more efficient adsorption and mass loading on the sensor surface. However, a further increase in temperature to 45°C appears to have a detrimental effect on the sensor's performance. The frequency shift at this temperature is less pronounced than 35°C, suggesting that excessively high temperatures may disrupt the intermolecular interactions or cause structural changes in the Schiff base nano cadmium complex, reducing binding affinity towards cadmium ions. These observations highlight the importance of optimizing the operating temperature for the QCM-based sensor employing the Schiff base nano cadmium complex. An appropriate temperature range, such as around 35°C in this case, can enhance the sensor's performance by promoting favorable intermolecular interactions and increasing the kinetics of cadmium ion binding. However, excessively high or low temperatures may adversely affect the sensor's sensitivity and response time, necessitating careful temperature control during practical applications.

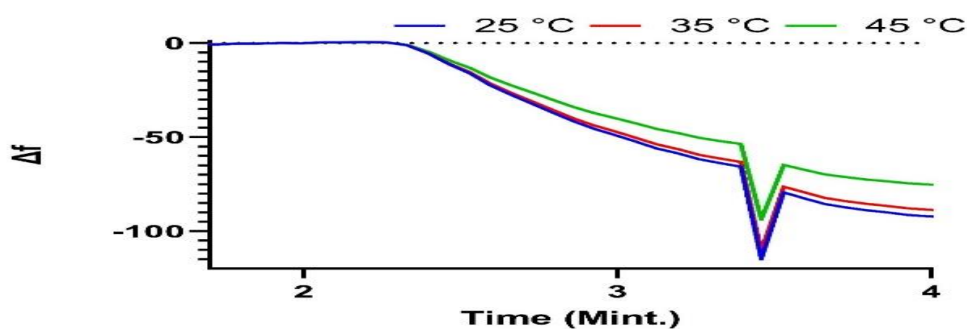


Fig 8. Effect of Temperature on the QCM Response of Schiff Base Nano Cadmium Complex

3.2.9. Effect of Ph

Figure 9 illustrates the influence of pH on the QCM-based sensor's response to cadmium ion detection. Three different pH values, 4, 7, and 10, were evaluated to assess the effect of pH on the sensor's performance (Fig 9) [78-79]. The graph depicts the changes in resonance frequency (Δf) over time for the Schiff base nano cadmium complex at these different pH conditions. At pH 4, a significant decrease in the resonance frequency is observed, indicating efficient binding of cadmium ions to the Schiff base nano cadmium complex. This behavior can be attributed to the favorable electrostatic interactions between the positively charged cadmium ions and the negatively charged functional groups in the nano cadmium complex at acidic pH conditions. As the pH increases to 7 (neutral conditions), a slightly less pronounced frequency shift is

observed, suggesting a minor reduction in the binding affinity of the Schiff base nano cadmium complex towards cadmium ions. This could be due to changes in the protonation states of the functional groups, leading to a slight decrease in the electrostatic interactions. However, at pH 10 (alkaline conditions), a significant reduction in the frequency shift is observed, indicating a substantial decrease in the binding of cadmium ions to the Schiff base Nano cadmium complex. This behavior can be attributed to the competition from sodium ions (Na^+) in the alkaline medium [80, 81]. At higher pH values, the concentration of sodium ions increases, and they can compete with cadmium ions for the available binding sites on the nano cadmium complex surface. This competition can lead to reduced adsorption of cadmium ions, resulting in a lower frequency shift observed in the QCM response. It is important to note that the Schiff base nano cadmium complex may possess specific molecular recognition sites or functional groups that exhibit selective binding towards cadmium ions over other interfering ions, such as sodium ions. However, at higher pH values, the increased concentration of sodium ions can overwhelm these selective binding sites, reducing sensitivity towards cadmium ions. These observations highlight the importance of optimizing the pH conditions for the QCM-based sensor employing the Schiff base nano cadmium complex. Acidic or neutral pH conditions may be more favorable for efficient cadmium ion detection, as they minimize the competition from interfering ions and maximize the electrostatic interactions between the nano cadmium complex and the cadmium ions.

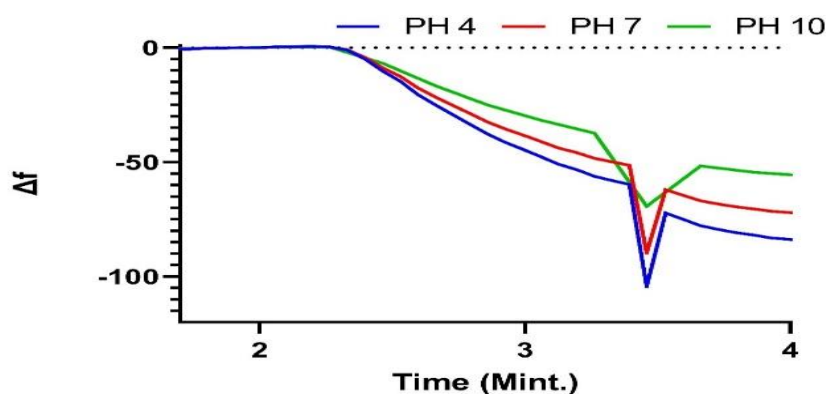


Fig 9. Effect of pH on the QCM Response of Schiff Base Nano Cadmium Complex towards Cadmium Ions

4. Conclusion

The research detailed in this paper describes the development of a novel nanoparticle-based QCM sensor system for the rapid and sensitive detection of cadmium (Cd) ions. The researchers synthesized the Nano Cd(II) Schiff base complex, extensively characterized using various analytical techniques such as DLS, zeta potential analysis, AFM, FT-IR, contact angle measurements, BET surface area determination, and pore size analysis. This comprehensive characterization provided valuable insights into the physiochemical properties of the nanoparticles. The feasibility of using the Nano Cd(II) complex as a QCM sensor was investigated, and the QCM sensor demonstrated excellent sensitivity, with the ability to detect Cd(II) ions at concentrations as low as 0.1 ppm. This ultra-low detection limit is a significant achievement compared to traditional analytical methods. The sensor's performance was evaluated under different pH and temperature conditions, showcasing its robustness and reliability for environmental monitoring applications. Cytotoxicity studies were conducted to assess the potential toxic effects of the Nano Cd(II) complex, an essential consideration for real-world sensor deployment. The developed sensor system could detect Cd(II) ions in groundwater and industrial wastewater samples, demonstrating its practical utility for environmental surveillance and protection. In conclusion, this research has successfully developed a susceptible, selective, and cost-effective QCM-based sensor platform using Nano Cd(II) Schiff base complexes to rapidly and reliably detect cadmium contamination. This innovative sensing technology has the potential to significantly improve environmental monitoring efforts and contribute to the mitigation of the harmful impacts of cadmium pollution. The sensor's ability to detect cadmium at very low concentrations makes it an invaluable tool for environmental monitoring, allowing for the early detection of cadmium pollution in water bodies, soil, and industrial effluents. This early detection is crucial for initiating timely interventions to prevent the spread of contamination and mitigate its adverse effects on ecosystems and human health. By providing continuous, real-time monitoring, the sensor ensures that environmental standards are met and helps maintain the safety and quality of natural resources. In pollution mitigation, the sensor's deployment in industrial settings can facilitate monitoring cadmium emissions and effluents, ensuring that industries comply with environmental regulations and reduce their environmental footprint. The sensor's robustness and reliability across various conditions make it suitable for diverse environmental applications, including monitoring cadmium levels in agricultural fields, thereby protecting food safety and public health. Furthermore, the implications of this technology extend beyond environmental applications. The sensor could be adapted to monitor drinking water quality, preventing cadmium exposure and its associated health risks. Its application in industrial process control can lead to more efficient management of heavy metal pollutants, promoting sustainable industrial practices. Developing the Nano Cd(II) Schiff base complex sensor significantly advances environmental

monitoring technology. Its high sensitivity, selectivity, and adaptability not only enhance environmental surveillance but also contribute to global efforts in pollution mitigation, ultimately promoting a healthier and more sustainable environment.

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