

Cadmium detection with nickel complex nanoparticles sensor using QCM technique

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Abstract: Cadmium (Cd) contamination in both water and soil constitutes a significant environmental concern, acknowledged as a pollutant. The uptake and accumulation of bioavailable Cd by food crops further accentuate its threat. The imperative for consistent monitoring of Cd levels in the environment stems from the aim of mitigating potential harm and exposure to humans. In this context, the synthesis of nickel complex nanoparticles emerges as an eco-friendly and dependable process, holding relevance across diverse domains. This process has led to the development of an innovative nano nickel sensor for the purpose of detecting cadmium. The comprehensive characterization of the nano nickel complex was accomplished through a different analytical tools, encompassing DLS, Zeta potential, TEM, AFM, FT-IR spectroscopy, contact angle measurements, BET surface area determination, and pore size analysis. Moreover, the application of the nano nickel complex as a simple, cost-effective, and highly sensitive QCM sensor was explored, primarily targeting the rapid detection of cadmium. Through the utilization of the nano nickel complex sensor as a discerning and responsive QCM sensor, cadmium detection can be achieved at concentrations as low as 1 ppm. The cytotoxicity of the cadmium complex nanoparticles was screened. Notably, this methodology exhibits successful applicability for the determination of Cd(II) ions in groundwater and industrial effluent wastewater samples, providing a valuable tool for environmental monitoring and protection.

Keywords: Nano sensor; cadmium; QCM; TEM; BET

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I. INTRODUCTION

Environmental pollution caused by cadmium (Cd) is a global concern due to its persistence, ability to bioaccumulate, and highly toxic nature [1-5]. Cd and its various compounds, whether as settled, soluble, bioadsorbed, or bioaccumulated forms, pervade the ecosystem. Therefore, the determination of bioavailable Cd plays a pivotal role in assessing health risks associated with Cd pollution [6-9]. Cadmium finds widespread application in industrial processes such as battery production, alloy formulation, coloring agents, and electroplating products. Additionally, it is commonly found in fertilizer manufacturing involving phosphate minerals and sewage sludge. Unfortunately, the extensive usage of this element comes with adverse impacts on both human health and the environment. Cadmium can accumulate in organs such as the kidney, thyroid gland, and spleen, leading to physiological disorders like renal dysfunction, calcium metabolism disturbances, and an increased susceptibility to specific cancers [11, 12].

Nanoparticles-based sensors have proven to be effective complements to instrumental methods, offering robust tools for predicting the accumulation, translocation, and ecotoxicological effects of heavy metal pollution [10]. Among various methods employed for toxic metal ion detection, the nanoparticles-based QCM sensor has gained substantial attention due to its advantages including low cost, selectivity, sensitivity, and rapid response time [13, 14]. Consequently, there exists a pressing need for a rapid, reliable, and highly sensitive sensor tailored for the detection of cadmium [15].

The principal objective of our ongoing research is to devise a unified analytical sensor capable of effectively detecting heavy metals, particularly cadmium ions.

II. MATERIALS AND METHODS

2.1. Preparation of Nano nickel complex

The nano nickel complex was synthesized through the cocadmium ionsination process. Initially, a hot ethanolic solution at 70°C containing the Schiff base ligand Fig (1) (1 mmol, 0.442 g) was prepared. In a separate hot absolute ethanol solution (20 ml), the metal salt (0.237 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) was dissolved. After three hours of continuous stirring under reflux conditions, the resulting complex began to precipitate from the solution. These precipitates were subsequently collected via filtration, subjected to thorough washing, and finally dried under a vacuum using anhydrous calcium chloride. The purification process was completed through recrystallization. Additionally, the formed complex underwent ultrasonic probe treatment for 10 minutes. Remarkably, during this procedure, the color of the complex transformed from green to brown. [16-18].

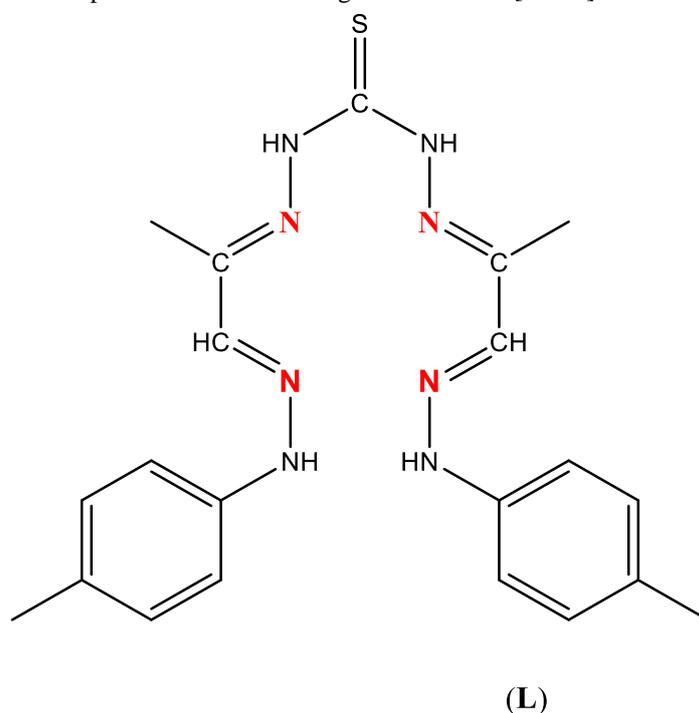


Fig 1.Schiff base ligand (L)

Instrumentation.

The microanalysis of carbon, hydrogen, and nitrogen was conducted using a CHNS-932 (LECO) Vario Elemental Analyzer at the Microanalytical Center, Cairo University, Egypt. The melting point determination was carried out using a Triforce XMTD-3000 instrument. Fourier Transform Infrared (FT-IR) spectra were obtained with a Perkin-Elmer 1650 spectrometer, employing KBr disks within the range of 4000–400 cm^{-1} . The molar conductance of solid complex solutions in ethanol at concentrations of 10^{-3} M was measured using a Jenway 4010 conductivity meter. Mass spectra were acquired via an MS-5988 GS-MS Hewlett-Packard instrument employing the electron ionization method at 70 eV. UV-Vis spectra of solutions were obtained using a Perkin-Elmer Model Lacadmium ionsda 20 automated spectrophotometer within the wavelength range of 200 to 700 nm. The research on antimicrobial properties was conducted at the Microanalytical Center, Cairo University. Cytotoxicity studies were carried out at the National Cancer Institute, Cairo University[19].

The surface charge and particle size of the nano nickel complex were determined using a ZetaSizer instrument (NanoSight NS500, Malvern Panalytical, Malvern, UK). Surface area and pore volume were analyzed with a surface area and pore volume analyzer (Quanta Chrome, Nova Touch 4L, USA) to determine the BET surface area using the multi-point and DH pore volume method. The metal complex nanoparticles were degassed at

65°C for 1.25 hours. Further examination of the prepared samples was conducted with a TEM instrument (JEOL, JEM-2100 high-resolution, Peabody, MA, USA). AFM studies were performed using an AFM instrument manufactured by Oxford (model Jupiter XR AFM) to determine the morphology of nickel complex nanoparticles. Prior to TEM analysis, the samples were sonicated for 10 minutes 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. Thin film synthesis was carried out using a Spin coater instrument (Laurell-650Sz, France) under vacuum conditions, with a speed of 750 rpm and a rate of 50µm per 120 seconds. AFM images and roughness profiles were measured at a size of 47 nm X 47 nm, utilizing a gold tap, contact mode, and a speed of 0.31 In/S. Wettability measurement was performed using a Biolin Scientific (model T200) contact angle analyzer under sessile drop conditions, with a measurement time of 10 seconds and a droplet volume of 4 µm of distilled water[20].

Establishing of QCM-Based nickel complex Nanosensors.

The QCM sensor utilized in this study consisted of an AT-cut quartz crystal chip with a gold electrode, measuring 12 mm in diameter and resonating at 5 MHz (Q-Sense, Shenzhen, China)[21].

Before the nanomaterial stabilization process, the gold sensor underwent a thorough cleaning procedure. It was immersed in a solution of aqueous ammonia, H₂O₂, and double-distilled water in a volumetric ratio of 5:1:1. The cleaning solution was maintained at 75°C, and the gold sensor was soaked for 10 minutes. Subsequently, the sensor was rinsed successively with double-distilled water and ethanol, and then allowed to air-dry at room temperature.

The dried quartz crystal chip was carefully inserted into the Q-Sense instrument. Initially, a stream of double-distilled water was introduced over the electrode to function as a background electrolyte. This step served to establish baseline measurements before introducing the sensor's nanomaterials. The continuous flow of double-distilled water was maintained in the QCM module until the QCM signal reached a steady state, at which point the signal value was recorded as zero.

Following the baseline measurement, a solution comprising 2 mL of 2 ppm nickel complex nanoparticles and 10 mL of double-distilled water was prepared. An aliquot of this mixture was then introduced to the gold sensor using a flow rate of 0.4 mL/min[22].

QCM-Monitoring of cadmium ions

The QCM measurements were conducted utilizing a QCM system (Q-senses, Biolin Scientific, Linthicum Heights, MD, USA)[23]. Each QCM measurement involved the injection of 1 ppm cadmium solutions onto the surfaces of QCM-based nickel complex nanosensors at varying temperatures (25°C, 35°C, and 45°C) and different pH levels (4, 7, and 10). The cadmium solution was introduced repeatedly until the signal reached a steady state, indicating that the binding interaction between the nanosensors and cadmium ions had reached equilibrium Fig (2). To remove unadsorbed particles from the surfaces of the QCM sensors, double-distilled water was once again introduced into the module after a predetermined period[24].

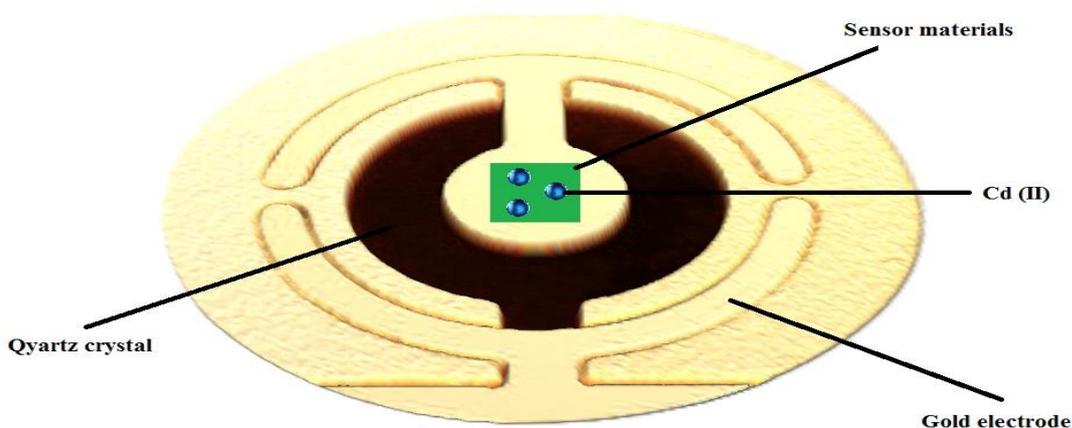


Fig. 2. illustrates the sensitivity of nickel complex nanoparticles to Cd(II) detection using the QCM-based sensor evaluation method.

III. RESULTS AND DISCUSSION

Characterization of nickel complex nanoparticles

a. Chemical Composition and Biological Properties of Nano Nickel Complex

The Nano nickel complex is known for its air-stability and solubility in polar organic solvents such as MeOH, DMF, and DMSO. However, it remains insoluble in water. Elemental analysis confirms a metal/ligand ratio of 1:1. The molar conductivity (Λ_m) values of the nickel complex in DMF (10^{-3} M) at 25°C were determined to be $105 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$, indicating its electrolytic nature. Comparative analysis of the infrared spectra of the parent ligand and the corresponding nickel complex offers insights into the coordination mechanism of the ligand toward the nickel center. Specifically, the azomethine group displayed a strong distinctive band at 1563 cm^{-1} , shifted to 1552 cm^{-1} in the complex, indicating coordination through the nitrogen atoms of the azomethine groups [25]. Non-ligand bands of the nickel complex were observed in the range of 409 cm^{-1} corresponding to $\nu(\text{M-N})$. The Ni(II) chelate demonstrated a multi-step decomposition process. Based on the data, the suggested formula for the nickel complex is $[\text{NiL}]\text{Cl}_2$. Notably, the nickel complex exhibited strong characteristic bands at 287nm, and 320 nm, corresponding to $\pi-\pi^*$ and $n-\pi^*$ intramolecular transitions [26].

The antimicrobial properties of the Nano nickel complex were assessed using the disc diffusion method. The complex was tested against a variety of bacterial and fungal strains, including Gram-positive bacteria (*Bacillus subtilis*, *Streptococcus faecalis*, *Staphylococcus aureus*), Gram-negative bacteria (*Escherichia coli*, *Pseudomonas aeruginosa*, *Neisseria gonorrhoeae*), and fungal strains (*Candida albicans*). The results indicated that the complex exhibited strong efficacy against both Gram-positive and Gram-negative bacterial strains. Additionally, the Nano Ni(II) complex displayed potent antifungal activity against *Candida albicans*.

A. Textural characters (TEM and AFM) of nickel complex Nano particles

The transmission electron microscopy (TEM) analysis of the nickel complex revealed the uniform dispersion of the synthesized particles, arranging themselves into well-defined spherical structures with diameters measuring less than 100 nm Fig. 4. Furthermore, the surface morphology of the synthesized nano nickel complex was meticulously examined using an atomic force microscope (AFM). The AFM images distinctly displayed a fibrous morphology Fig. 3., showcasing the absence of any visible indications of aggregation or agglomeration. The particle size derived from the AFM images was determined to be below 40 nm.

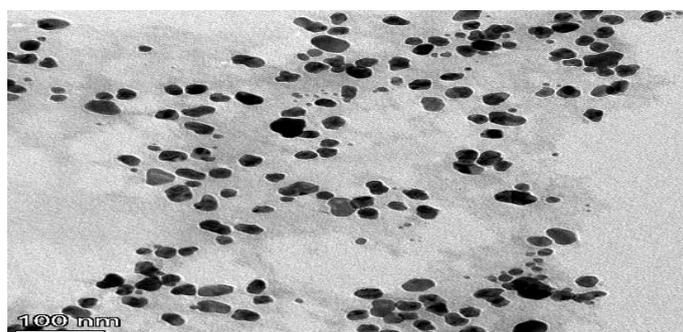
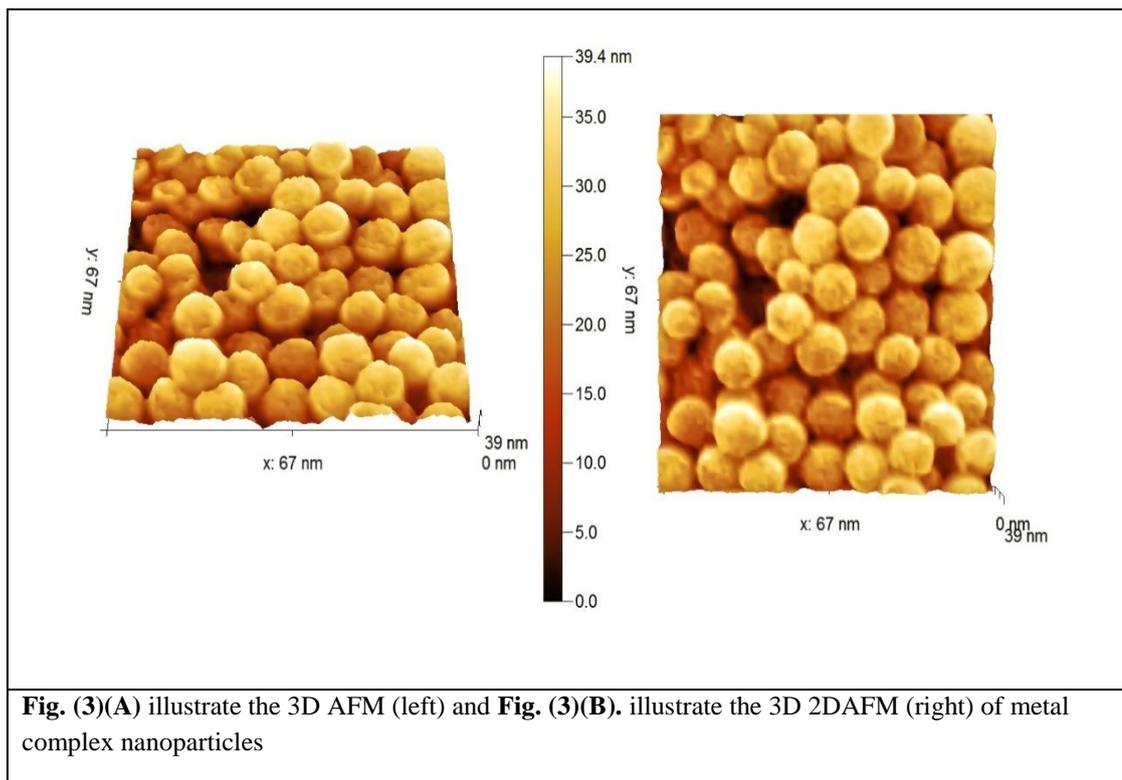


Fig. 4. illustrates the TEM images Reveals Well-Defined Spherical Structures of Nickel Complex Nanoparticles.

B. DLS and Zeta Potential

The determination of the particle size of the nano nickel complex was carried out using dynamic light scattering (DLS) technique, as depicted in Fig (5). The nano nickel complex exhibited an average particle size of 27 nm . Notably, the obtained results revealed that the suspension of the nano nickel complex exhibited a unimodal size distribution and displayed a high degree of colloidal stability .

The particle size distribution and Zeta potential outcomes of the nano nickel complex are illustrated in Fig.6. The Zeta potential was measured to be -21 mV, signifying a well-dispersed state of the nanoparticles . Zeta potential is a crucial parameter that reflects the physicochemical stability of nanoparticles, particularly during storage conditions [27]. A higher absolute value of Zeta potential indicates a more stable system [28]. The substantial negative Zeta potential value of the nano nickel complex further confirms its high stability [27, 28].

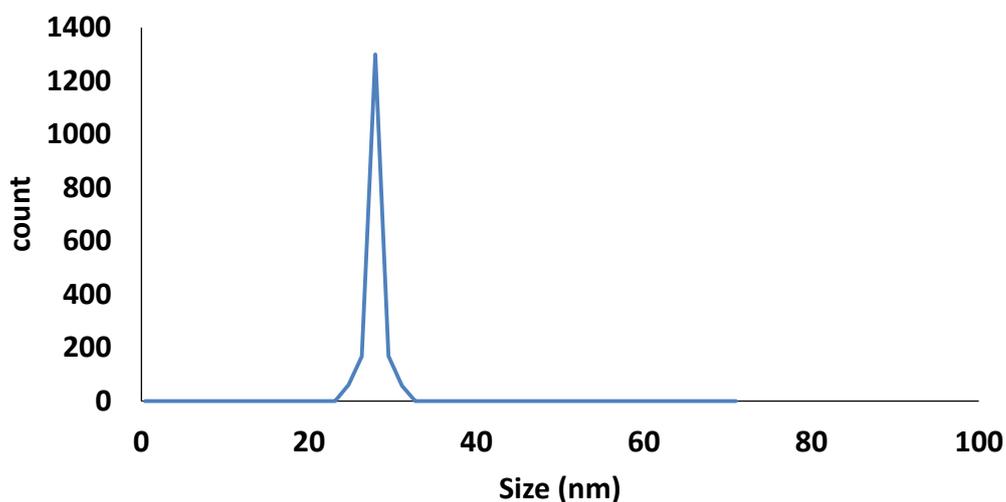


Fig .5. illustrates the Particle Size Analysis of Nano Nickel Complex by Dynamic Light Scattering (DLS): Uniform Unimodal Distribution and Colloidal Stability.

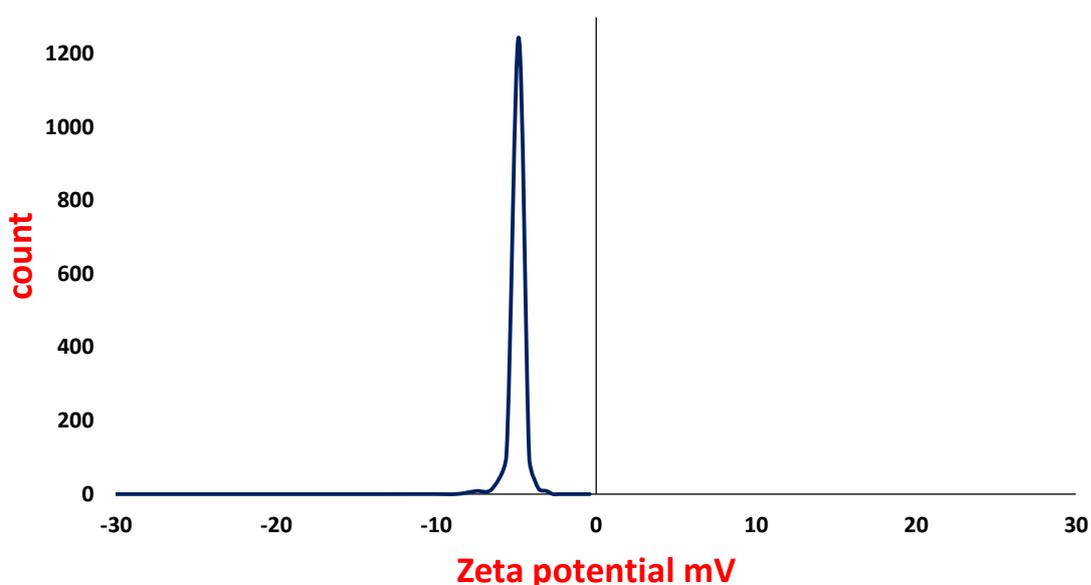


Fig .6. illustrates the Visualization of Particle Size Distribution and Zeta Potential of Nano Nickel Complex.

C. BET surface area and pore size.

The Brunauer-Emmett-Teller (BET) method, named after its creators Brunauer, Emmett, and Teller, is a valuable technique for characterizing nanoscale materials. This method relies on the physical adsorption of a gas on a solid surface and is commonly used to determine the surface area of nanostructures due to its efficiency and simplicity [29].

Utilizing BET adsorption isotherms, the surface area characteristics of the nano nickel complex sample were assessed, as illustrated in Fig.7. [29]. Following De Boer's classification, which categorizes hysteresis loop isotherm curves into four types to elucidate porous structure, it was revealed that all samples of nickel complex nanoparticles exhibited type IV nitrogen adsorption-desorption isotherms accompanied by hysteresis loops, confirming their macroporous nature [29]. The multipoint BET surface area was determined to be $60.3 \text{ m}^2/\text{g}$, with a corresponding pore volume of $18.1 \text{ cc}/\text{nm}$ by the DH method [29]. The substantial multipoint BET surface area contributes to the heightened adsorption capacity of metal complex nanoparticles for cadmium ions in aqueous solutions [29]. Additionally, the presence of a macroporous structure can be attributed to the fiber morphology of the metal complex nanoparticles [29].

The existence of macroporosity further enhances the adsorption of cadmium ions onto the surface of the metal complex nanoparticles [29]. This unique attribute augments their potential as efficient adsorbents for cadmium ion removal from aqueous solutions [29].

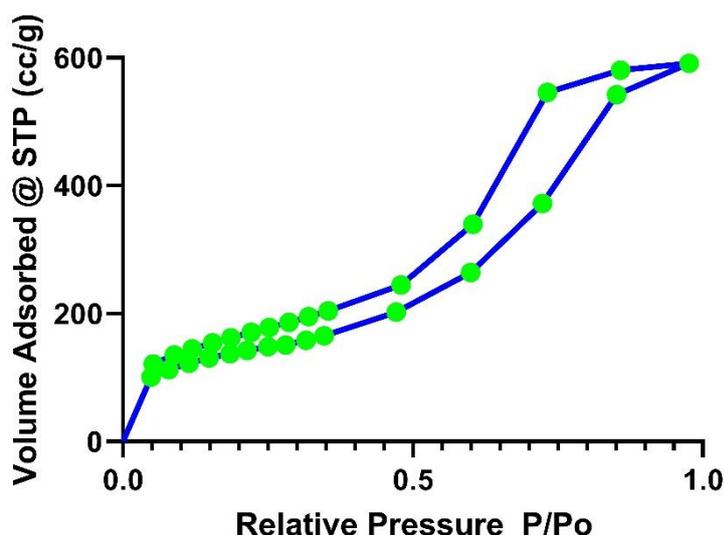


Fig .7. illustrates the Surface Area Characterization of Nano Nickel Complex via N_2 Adsorption-desorption Isotherm

D. Contact angle, Hydrophobicity and toxicity of nickel nano complex

The nano nickel complex particles exhibited strong hydrophobic characteristics, as evidenced by a water contact angle of 111° . This hydrophobic nature significantly bolsters the utility of these nanoparticles as effective sensors in water environments.

When designing environmentally friendly nanoparticle-based sensors, it is imperative to ensure the non-toxic nature of the materials employed. The cytotoxicity of the nano nickel complex was rigorously evaluated, revealing an IC_{50} value of $180 \mu\text{g}/\text{ml}$. This relatively high IC_{50} value provides a positive indication of the low cytotoxicity of the nano nickel complex, further encouraging its application as a sensor in water-related contexts.

E. Cadmium ions Monitoring Using QCM-Based Nano nickel sensors

A typical series of QCM-based experiments with the nano nickel complex sensor can be outlined in four distinct stages:

Baseline Stability (Stage 1): At this stage, the frequency response of the nanosensors is recorded, establishing a stable baseline for subsequent measurements.

Initial Binding (Stage 2): A sudden drop in frequency change is observed, attributed to the rapid binding of cadmium ions to the sensors. This phenomenon could be attributed to the availability of numerous vacant sites on the sensor's surfaces that enable the swift binding process.

Enhanced Adsorption (Stage 3): The binding process continues, leading to further adsorption of Cadmium ions molecules onto the sensor surfaces. This stage is characterized by an additional increase in frequency change.

Equilibrium State (Stage 4): A point is reached where the frequency shift stabilizes after the addition of the nano nickel complex but before the introduction of Cadmium ions solution. This signifies the attainment of equilibrium in the adsorption process between the nano nickel complex and Cadmium ions molecules.

Upon the introduction of Cadmium ions, a significant and rapid change in frequency is observed, indicating the adsorption of these ions onto the surface of the QCM-based nickel complex nanosensors. This response highlights the sensor's capability to effectively bind Cadmium ions molecules .

Once a stable frequency is re-established, it signifies that an equilibrium state has been achieved, where Cadmium ions adsorption on the surface of the QCM-based nano nickel complex sensor has reached a balance. During this equilibrium, minimal changes in the frequency of the sensors are observed, suggesting that only minor mass loss and minor structural modifications have occurred on the nanosensor surfaces .

The outcomes demonstrate that the QCM-based nano nickel complex sensor is proficient in detecting Cadmium ions, offering an effective tool for such applications.

F. Proposed Sensing Mechanism of the QCM-Based nano nickel complex.

The interaction mechanisms between Cadmium ions and the nano nickel complex sensor involve various factors driven by their respective electronic properties. Cadmium ions, with lower electronegativity, exhibit distinctive interactions with the nano nickel sensor.

The presence of dipole-dipole interactions might arise from the unequal sharing of electrons in Cadmium ions and the nano nickel sensor. This phenomenon could lead to the establishment of dipole interactions, where electron clouds of both entities align in parallel, further influencing their binding.

Furthermore, the nano nickel complex contains polar side chains that function as electron donors. These side chains contribute to an increased density of negative charge on the surface of the nano nickel complex. As a result, the QCM-based nano nickel sensor becomes more prone to interacting with Cadmium ions. This interaction encompasses not only electrostatic attractions due to the presence of opposite charges but also enhanced π - π interactions, synergistically driving the binding process.

The interplay of these interaction mechanisms—dipole-dipole interactions, π - π interactions, and electrostatic attractions—adds to the complexity of the binding phenomenon between Cadmium ions and the nano nickel complex sensor, resulting in a comprehensive and multifaceted interaction profile.

G. Effect of temperature on the sensor performance

Temperature exerts a significant impact on chemical reactions, leading to enhancements or inhibitions based on the reactants' and products' surroundings. This influence is particularly pronounced due to the interplay between the reaction and its environment. Alterations in temperature trigger accelerated diffusion of the adsorbate molecules through both the exterior boundary layer and internal pores of the adsorbent material Fig. 8.

Moreover, temperature adjustments augment the adsorbent's ability to achieve equilibrium with a specific adsorbate, further influencing the overall adsorption process. In light of these principles, the effect of temperature on the monitoring of Cadmium ions was explored. This study involved assessing different temperatures 25°C, 35°C, and 45°C utilizing the nano nickel complex sensor. The results, as depicted in the Fig(8), underscore the intricate relationship between the medium's temperature and the sensitivity of Cadmium ions detection in aqueous solutions Fig(8).

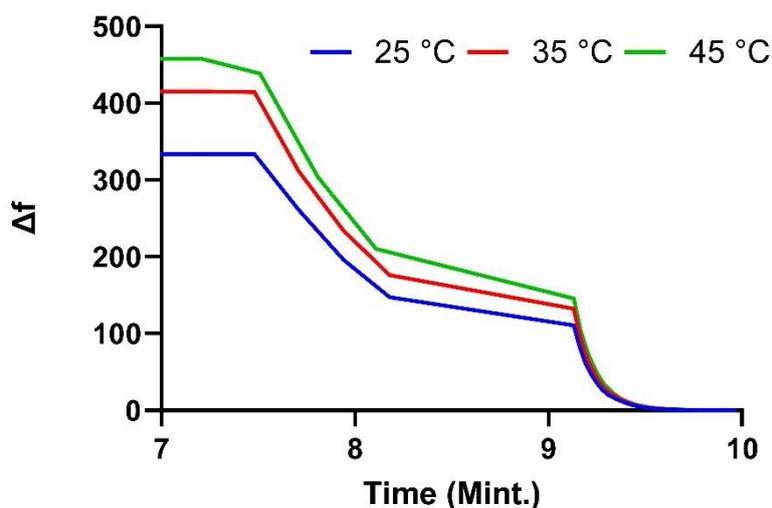


Fig .8. Temperature-Dependent Sensitivity of CADMIUM IONS Detection Using Nano Nickel Complex Sensor.

The observed phenomenon revealed an intriguing relationship between temperature and the adsorption behavior of Cadmium ions on the QCM-based nano nickel sensor. Surprisingly, as the temperature increased from 25°C to 45°C, there was a noticeable increase in the frequency shifts a counterintuitive trend in contrast to the typical behavior observed in the QCM-based nano nickel sensor, where frequency shifts tend to increase. This divergence can be attributed to the nature of the interaction between the QCM-based nano nickel sensor and the cationic Cadmium ions.

This interaction is rooted in electrostatic attraction, where the highly negatively charged surface of the QCM-based nano nickel sensor binds with the positively charged Cadmium ions. With rising temperature, Cadmium ions tend to diffuse more extensively within the solution, potentially diminishing their attachment to the QCM-based nano nickel sensor's surface. Furthermore, the increased temperature could lead to bond splitting of the sensor's reactive groups on the surface, thereby reducing the availability of active adsorption sites for Cadmium ions.

Interestingly, the impact of temperature on the adsorption of metal ions was consistent with this trend, revealing a decrease in metal ion adsorption with higher temperatures. This trend was further supported by the observation that the adsorption of CADMIUM IONS onto the QCM-based nano nickel sensor's surface resulted in significant frequency changes, which can be attributed to the mass of Cadmium ions adsorbed onto the sensor.

H. Effect of different pH on the sensor performance

The initial pH value of the sorbent significantly influences metal adsorption due to its impact on the chemical speciation of metal ions within the sorbate and the ionization of functional groups on the adsorbent surface[30]. To explore the pH-dependent adsorption of cadmium ions, a series of batch experiments were conducted at distinct pH values (4, 7, and 10) [30]. As illustrated in Fig .9., the highest adsorption capacity on the adsorbents was observed within the pH range of 4 to 6, followed by a pronounced reduction with decreased pH values and a marginal decrease at elevated pH values [30].

Elevated pH levels lead to the precipitation of cadmium ions as hydroxides, leading to a decrease in adsorption Fig. 9. [30]. This phenomenon can also be attributed to the increased presence of Na⁺ ions resulting from pH adjustments, which compete with the remaining cadmium ions for exchangeable sites [30-33].

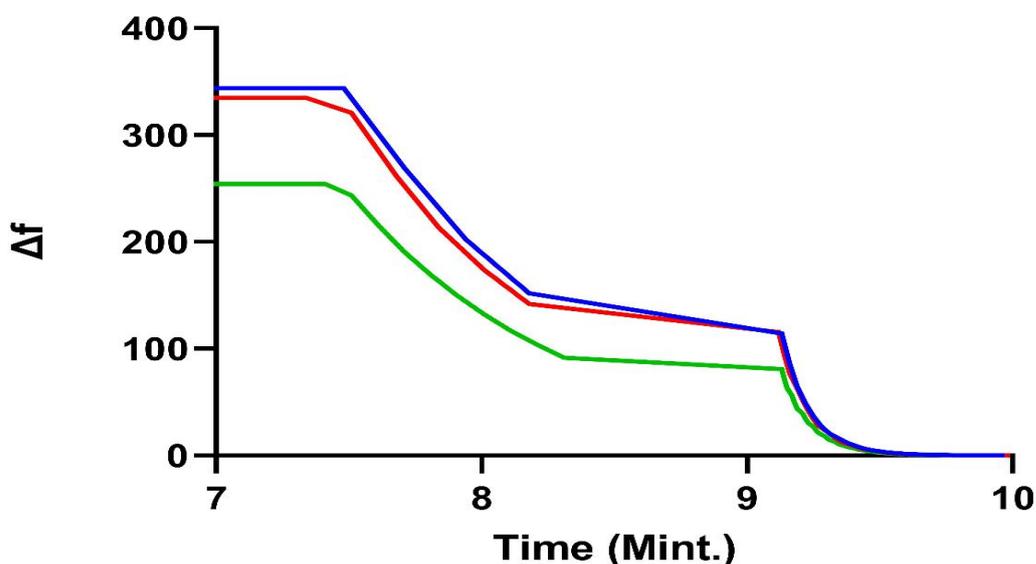


Fig .9. Effect of different pH on the performance of nano nickel complex QCM sensor (green pH=4, red pH=7, pH = 10)

V –CONCLUION

In this study, we have successfully developed a novel nano nickel sensor for the reliable detection of Cadmium ions present in water streams. The characterization of the nano nickel sensor using DLS and Zeta potential measurements highlighted its particle size distribution of approximately 27 nm, along with a zeta potential of -21 mV. Furthermore, the utilization of TEM and AFM imaging techniques revealed the presence of a spherical structure within the nanosensor.

Subsequently, the synthesized nanomaterials were harnessed as innovative nanosensors employing the QCM method. These engineered nanosensors were then applied to monitor low concentrations of Cadmium ions, with levels around 1 ppm. This monitoring was carried out across various temperatures (25 °C, 35 °C, and 45 °C) and pH values (4, 7, and 10). The outcomes underscored the efficacy of the QCM-based nickel complex nanoparticles as a valuable tool for real-time, rapid, and sensitive detection of Cadmium ions. Notably, the nanosensor exhibited a rapid response time of approximately 7 minutes. This versatile nanosensor demonstrates its potential for applications in continuous-flow water streams and diverse environmental samples, making it an essential instrument for monitoring Cadmium ions in different scenarios.

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