



## DESIGN AND CHARACTERIZATION OF NANO COBALT COMPLEX AS LOW LIMIT DETECTION QCM SENSOR FOR CADMIUM IONS

Emam M. Komyha<sup>1</sup>, Walaa H. Mahmoud<sup>1</sup>, Wafaa M. Hosny<sup>1</sup> and Ahmed A. El-Sherif<sup>1</sup>

<sup>1</sup>Department of Chemistry, Faculty of Science, Cairo University, Egypt



### Abstract

Cadmium (Cd) contamination in water and soil is widely recognized as a significant environmental pollutant. The potential for food crops to absorb and accumulate bioavailable Cd has raised concerns about human exposure and associated health risks. Continuous monitoring of Cd levels in the environment is crucial to minimize potential harm to humans. The synthesis of metal complex nanoparticles presents an eco-friendly and dependable approach that finds applications in various fields.

A recent development involves the creation of a novel nano cobalt sensor specifically designed for the detection of cadmium. The nano cobalt complex was thoroughly characterized using a range of analytical techniques, including Dynamic Light Scattering (DLS), Zeta potential analysis, Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM), Fourier-Transform Infrared Spectroscopy (FT-IR), contact angle measurements, BET surface area analysis, and pore size determination. These comprehensive characterizations provide essential insights into the nano cobalt complex's structure and properties.

Furthermore, this nano cobalt complex was harnessed as a simple, cost-effective, and highly sensitive Quartz Crystal Microbalance (QCM) sensor for the rapid detection of cadmium. Using this nano cobalt complex sensor, cadmium ions can be detected at remarkably low concentrations, as low as 1 ppm. Importantly, the cytotoxicity of the cadmium complex nanoparticles was thoroughly assessed to ensure their safety.

This innovative method has demonstrated its applicability in the determination of Cd(II) ions in diverse environmental samples, including groundwater and industrial effluent wastewater. Its selectivity and sensitivity make it a valuable tool for monitoring and managing cadmium contamination.

**Keywords:** Nano sensor; cadmium; QCM; TEM; BET; DLS.

### I. Introduction

Cadmium (Cd) contamination poses a significant global environmental concern due to its persistent nature, propensity for bioaccumulation, and highly toxic characteristics [1]. Cd and its various compounds exist in different forms, including settled, soluble, bio-adsorbed, or bio-accumulated, and are distributed throughout ecosystems. As a result, assessing the bioavailable Cd levels is crucial for evaluating health risks associated with Cd pollution [2].

Cadmium finds extensive use in various industrial processes, such as battery manufacturing, alloy production, coloring agents, and electroplating products. It is also commonly found in fertilizer production using phosphate minerals and sewage sludge. Unfortunately, the widespread use of this element has adverse effects on both human health and the environment. Cadmium tends to accumulate in organs like the kidneys, thyroid gland, and spleen, leading to physiological

disorders, including renal dysfunction, disturbances in calcium metabolism, and an increased incidence of certain cancers [3, 4].

Nanoparticle-based sensors have emerged as effective complements to instrumental methods, proving to be powerful tools for predicting the accumulation, translocation, and ecotoxicological impacts of heavy metal pollution [5]. Various methods have been employed to detect toxic metal ions, with nanoparticle-based Quartz Crystal Microbalance (QCM) sensors gaining significant attention due to their cost-effectiveness, selectivity, sensitivity, and rapid response times [6, 7]. Consequently, there is a pressing need for the development of a rapid, reliable, and highly sensitive sensor for detecting cadmium [8]. Our current research focus centers on the creation of a single analytical sensor capable of detecting heavy metals, particularly cadmium ions

\*Corresponding author e-mail: [aelsherif@sci.cu.edu.eg](mailto:aelsherif@sci.cu.edu.eg) (Prof. Dr. Ahmed El-Sherif)

Receive Date: 12 September 2023, Revise Date: 08 October 2023, Accept Date: 11 October 2023

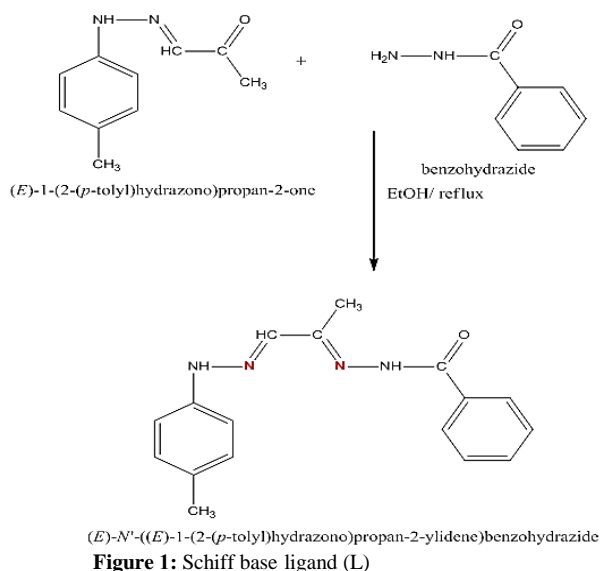
DOI: [10.21608/EJCHEM.2023.235176.8605](https://doi.org/10.21608/EJCHEM.2023.235176.8605)

©2024 National Information and Documentation Center (NIDOC)

## II. Materials and methods

### Preparation of Nano cobalt complex

To synthesize the Nano cobalt complex, a hot ethanolic solution (70°C) containing the Schiff base ligand Fig(1) (1 mmol, 0.29 g) was mixed with a hot absolute ethanol solution (20 ml) of the metal salt (0.23 g  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ )[9]. The mixture was stirred at reflux conditions for 3 hours, leading to the gradual precipitation of the complex. The resulting precipitates were separated through filtration, thoroughly washed multiple times, and then dried under vacuum conditions using anhydrous calcium chloride. The final purification step involved recrystallization, resulting in the formation of the pure metal complex. Subsequently, the complex underwent a 10-minute ultrasonic probe treatment, resulting in a color change from green to brown.



### A. Instrumentation

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 was determined using a triforme XMTD-3000 instrument. Fourier transform infrared (FT-IR) spectra were obtained using a Perkin-Elmer 1650 spectrometer, utilizing KBr disks in the range of  $4000\text{--}400\text{ cm}^{-1}$ . Molar conductance measurements of solid complex solutions in ethanol (at concentrations of  $10^{-3}\text{ M}$ ) were performed using a Jenway 4010 conductivity meter. Mass spectra were acquired through the electron ionization method at 70 eV using an MS-5988 GS-MS Hewlett-Packard instrument. A UV-Vis Perkin-

Elmer Model Lacadmium ionsda 20 automated spectrophotometer was employed to obtain solution spectra within wavelengths spanning 200 to 700 nm.

For the characterization of the nano cobalt complex [10], the surface charge and particle size were determined using a zeta sizer instrument (NanoSight NS500, Malvern Panalytical, Malvern, UK). The BET surface area was determined using a surface area and pore volume analyzer (Quanta Chrome, Nova Touch 4L, USA) with multi-point and DH pore volume methods. Prior to analysis, metal complex nanoparticles were degassed at 65°C for 1.25 hours. The prepared samples were further examined with a TEM instrument (JEOL, JEM-2100 high-resolution, Peabody, MA, USA), and AFM studies were conducted using an AFM instrument manufactured by Oxford (model Jupiter XR AFM) to assess the morphology of the cobalt complex nanoparticles. Prior to TEM analysis, the nanoparticles were sonicated for 15 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 Spain coater instrument (Laurell-650Sz, France) under vacuum conditions with a speed of 750 rpm and a drop rate of  $50\mu\text{m}$  per 120 seconds. AFM images and roughness profile measurements were performed with a size of  $47\text{ nm} \times 47\text{ nm}$ , utilizing a gold tap in contact mode at a speed of 0.31 In/S. Wettability measurements were conducted 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  $4\mu\text{m}$  of distilled water. Establishing of QCM-Based cobalt complex Nanosensors

The QCM sensor is contained an AT-cut quartz crystal chip attached to a gold electrode with a diameter of 12 mm, and a resonance frequency of 5 MHz (Q-Sense, Shenzhen, China).

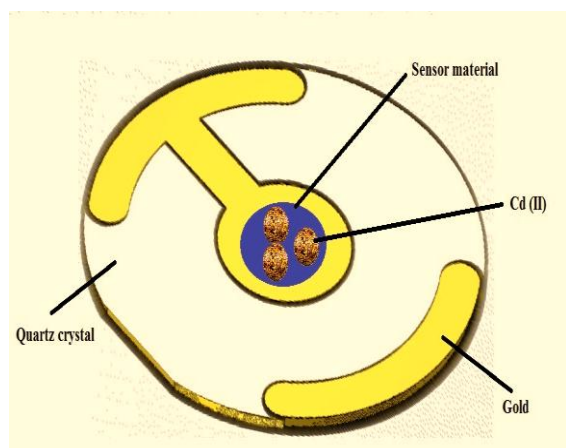
Prior to the stabilization of the nanomaterials, the gold sensor was cleaned by immersing it in a 5:1:1 v/v/v solution of aqueous ammonia,  $\text{H}_2\text{O}_2$ , and double-distilled water for 10 min at 75°C. Then, the gold sensor was rinsed with double-distilled water, and ethanol, and allowed to dry at room temperature. The dried chip was subsequently inserted into the Q-Sense instrument. Afterward, a stream of double-distilled water was first injected over the electrode to serve as a background electrolyte. Injecting the background electrolyte solution (double distilled water) into the QCM module enables the baseline measurements before adding the sensor's nanomaterials. In order to keep the QCM signal steady, the QCM module was

continuously fed by double-distilled water until the value of the QCM signal was then recorded as zero. Then, 2 mL of 2 ppm cobalt complex NPs 10 mL of double distilled water. Following that, aliquot of the mixture was flushed on the gold sensor at a flow rate of 0.4 mL/min.

### B. QCM-Monitoring of cadmium ions.

Utilizing a QCM system (QCM, Q-senses, Biolin Scientific, Linthicum Heights, MD, USA)[11], we conducted QCM measurements as part of our experimental procedure. For each measurement, we introduced 1 ppm cadmium solutions onto the surfaces of QCM-based cobalt complex nanosensors, varying the temperature conditions to 25°C, 35°C, and 45°C. Additionally, we explored different pH levels, specifically pH 4, pH 7, and pH 10 [12]. The cadmium solution was injected repeatedly until the signal achieved a stable state[13], signifying the attainment of equilibrium in the binding interaction between the nanosensors and the cadmium ions Fig.2.

To eliminate any unadsorbed particles adhering to the QCM sensor surfaces, we introduced double-distilled water into the module after a predetermined duration [14].



**Figure 2:** illustrate sense of cobalt complex nanoparticles for Cd(II) by QCM-based sensor evaluated method

## III. Result and discussion

### 1. Characterization of cobalt complex nanoparticles.

#### Chemical composition and biological properties of Nano cobalt complex

The nano cobalt complex under investigation possesses distinct properties. It is air-stable and readily soluble in polar organic solvents such as ethanol (EtOH), methanol (MeOH), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) [15]. However, it remains insoluble in water. Elemental analysis has confirmed a metal/ligand ratio of 1:2. Notably,

the molar conductivity ( $\Lambda_m$ ) value of the cobalt complex in DMF (at a concentration of  $10^{-3}$  M) at 25°C was determined to be  $41 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ , suggesting its non-electrolyte nature.

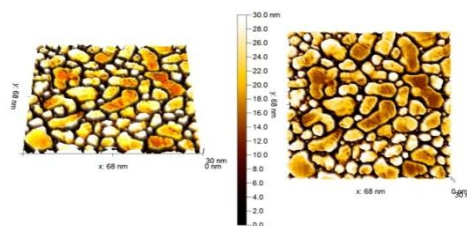
In order to elucidate the coordination mechanism of the ligand with the cobalt center, we compared the infrared spectra of the parent ligand and the resulting cobalt complex. Specifically, the azomethine group exhibited a distinctive strong band at  $1598 \text{ cm}^{-1}$  in the parent ligand, which shifted to  $1620 \text{ cm}^{-1}$  in the complex, indicating coordination through the nitrogen atoms of the azomethine groups [15]. In the infrared spectra, nonligand band was observed in the range of  $421 \text{ cm}^{-1}$  corresponding to  $\nu(\text{M}-\text{N})$  vibrations. Based on this data, the suggested formula for the cobalt complex is  $[\text{Co}(\text{L})_2\text{Cl}_2]$  [15].

In the ultraviolet region, the cobalt complex exhibits strong characteristic bands at 242 nm, 265 nm, and 358 nm, corresponding to  $\pi-\pi^*$  and  $n-\pi^*$  intramolecular transitions [16].

To assess its biological properties, the cobalt complex nanoparticles were subjected to antibacterial and antifungal testing using the disc diffusion method. Gram-positive bacteria (*Bacillus subtilis*, *Streptococcus faecalis*, and *Staphylococcus aureus*), Gram-negative bacteria (*Escherichia coli*, *Pseudomonas aeruginosa*, and *Neisseria gonorrhoeae*), and fungal strains (*Candida albicans* and *Aspergillus flavus*) were used as test organisms. The observed outcomes demonstrate the present analysis's complexes' efficacy against both Gram-positive and Gram-negative bacterial strains [17]. Only *Candida albicans* exhibited strong antifungal activity

### AFM of cobalt complex Nano particles

the surface morphology of the synthesized nano cobalt complex was meticulously examined using an Atomic Force Microscope (AFM). The AFM images vividly illustrate a rod shape morphology as depicted in Fig.3. and notably, there are no indications of aggregation or agglomeration present. The particle size deduced from the AFM images measures less than 30 nm [18].



**Figure 3:** illustrate the 3D AFM of cobalt complex nanoparticles.

## 2. DLS and Zeta Potential.

Utilizing the Dynamic Light Scattering (DLS) technique, we conducted an analysis to determine the particle size of the nano cobalt complex. The results unveiled that the nano cobalt complex exhibits an average particle size of approximately 25 nm. These findings further emphasize that the suspension of the nano cobalt complex displays a unimodal size distribution, characterized by low polydispersity indices, indicative of its exceptional colloidal stability.

For a comprehensive understanding of the particle size distribution and the electrostatic charge on the nano cobalt complex. The Zeta potential measurement revealed a value of -27 mV, signifying a uniform dispersion of the nanoparticles. It's important to note that Zeta potential plays a crucial role in gauging the physicochemical stability of nanoparticles during storage [19]. In general, a higher absolute value of Zeta potential corresponds to increased system stability [20]. Consequently, the observed Zeta potential of -27 mV underscores the high degree of stability exhibited by the nano cobalt complex.

## 3. BET surface area and pore size.

The BET (Brunauer, Emmett, and Teller) method, named after its pioneering creators, is a pivotal technique for characterizing materials at the nanoscale. It relies on the physical adsorption of gases onto solid surfaces and stands as a highly effective, rapid, and straightforward means of determining the surface area of nanostructures [21]. In our investigation, we harnessed BET adsorption isotherms to assess the surface area properties of the nano cobalt complex sample, as illustrated in Fig(4).

To delve into the porous nature of the material, we applied De Boer's classification, which categorizes isotherm curves based on the shape of the hysteresis loop. Remarkably, each sample of cobalt complex nanoparticles exhibited type IV nitrogen adsorption-desorption isotherms with hysteresis loops, unequivocally confirming their macroporous attributes.

The multipoint BET surface area was quantified at 69.8 m<sup>2</sup>/g, and the pore volume, determined via the DH (Dollimore-Heal) method, amounted to 21.5 cc/nm. This substantial multipoint BET surface area is of paramount importance, as it enhances the metal complex nanoparticles' capacity to adsorb cadmium ions in aqueous solutions.

The existence of macroporosity can be attributed to the presence of the fibrous morphology inherent to the metal complex nanoparticles. Notably, this macroporous structure plays a pivotal role in

elevating the adsorption potential of cadmium ions on the surface of the metal complex nanoparticles. This underscores their significance in applications related to environmental remediation and adsorption processes..

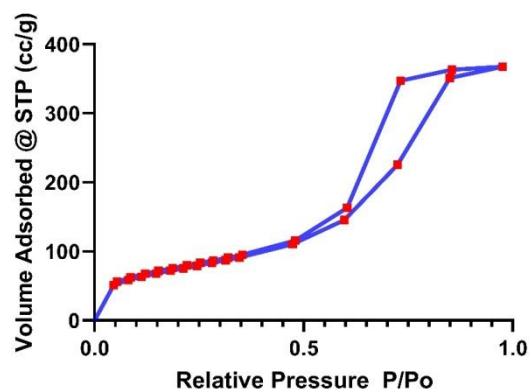


Figure 4: N<sub>2</sub> adsorption- desorption isotherm demonstrates the assessment of the surface area characteristics of the nano cobalt complex sample

## 4. Contact angle, Hydrophobicity and toxicity of cobalt nano complex.

The nano cobalt complex particles exhibited hydrophobic characteristics, evident from their water contact angle measuring 118° Fig (5) [22]. This inherent hydrophobicity in water greatly enhances the suitability of these nanoparticles for use as effective sensors in aquatic environments.

In the pursuit of developing environmentally friendly nanoparticle-based sensors, it's crucial to consider the material's toxicity. The toxicity assessment of the nano cobalt complex revealed an IC<sub>50</sub> value of 260 µg/ml [23]. This relatively high IC<sub>50</sub> value indicates that the nano cobalt complex is non-toxic at typical concentrations, further encouraging its use as a sensor in water-related applications.

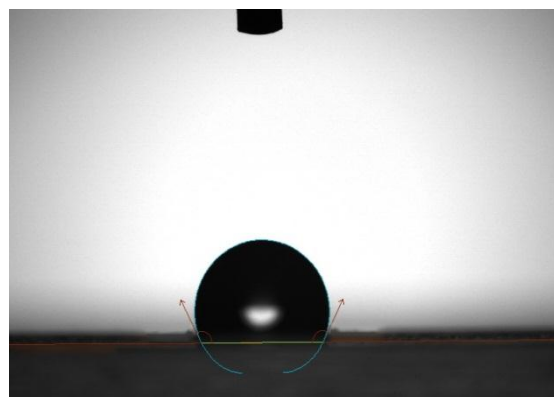


Figure 5: Water Contact Angle Measurement of Nano Cobalt Complex Particles

### 5. Cadmium ion Monitoring Using QCM-Based Nano cobalt sensors

A typical QCM-based nano cobalt complex sensor experiment consists of four stages. **First**, the frequency response of the nanosensors is measured to establish a stable baseline[24]. **In the second stage**, there is a sudden drop in frequency due to the rapid binding of cadmium ions with the sensors, which can be attributed to the large number of vacant sites on the sensor surfaces[24]. **The third stage** involves further adsorption of Cadmium ion, and **the fourth stage** represents the equilibrium state of the adsorption process between the nano cobalt complex and Cadmium ion [24]. Before introducing the Cadmium ion solution into the QCM system, the frequency shift remains steady after adding the nano cobalt complex. However, once Cadmium ion are adsorbed on the surface of the QCM-based cobalt complex nanosensors, a drastic change in frequency occurs [24]. This change indicates that the QCM-based Cobalt complex nanosensor is capable of binding Cadmium ion molecules and provides a noticeable response to their adsorption[24].

Once the frequency stabilizes again, it signifies that an equilibrium state of Cadmium ion adsorption on the surface of the QCM-based nano cobalt complex sensor has been reached[24]. At this point, no significant changes in the frequency of the sensors are observed, indicating minimal mass loss and only minor structural modifications on the nanosensor surfaces[24]. This suggests that the QCM nano cobalt complex sensor can effectively detect Cadmium ions [24].

### 6. Proposed Sensing Mechanism of the QCM-Based nano cobalt complex.

Due to the lower electronegativity of cadmium ions compared to the nano cobalt sensor, it is likely that dipole-dipole interactions come into play[25]. Moreover, the presence of polar side chains on the nano cobalt complex acts as functional groups with electron-donating properties, thereby enhancing the density of negative charge. Consequently, the QCM-based nano cobalt sensor is predisposed to interact more readily with cadmium ions, driven by electrostatic interactions [26].

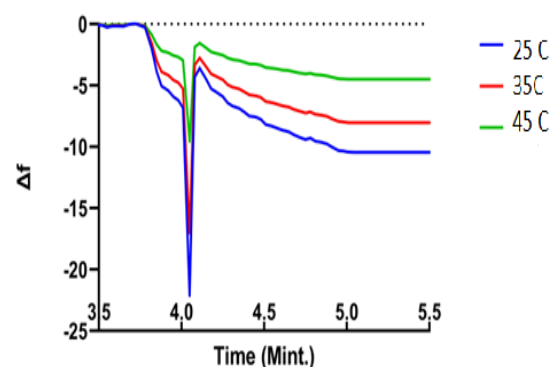
### 7. Effect of temperature.

Chemical reactions are notably influenced by temperature, often leading to either enhancement or inhibition of a particular reaction, depending on the environmental conditions surrounding the reactants and/or products [27]. In the context of adsorption processes, temperature plays a crucial

role. When temperature changes, the adsorbate molecules tend to diffuse more rapidly through the exterior boundary layer of the adsorbent and within its pores [28]. Furthermore, altering the temperature can significantly improve the adsorbent's ability to reach equilibrium with a given adsorbate [29].

To investigate the impact of temperature on the monitoring of cadmium ions ( $\text{Cd}^{2+}$ ), experiments were conducted at different temperatures, specifically 25°C, 35°C, and 45°C, utilizing the nano cobalt complex sensor [30]. The results, as depicted in Fig.6., clearly demonstrate that the sensitivity of detecting cadmium ions in aqueous solutions is influenced by the temperature of the medium.

For a more in-depth understanding and to explore the specific findings and mechanisms, I would recommend referring to relevant scientific literature on adsorption processes and the effect of temperature on chemical reactions in solution environments.



**Fig. 6.** Effect of Temperature on Cadmium Ion Detection Sensitivity in Aqueous Solutions Using Nano Cobalt Complex Sensor.

A noteworthy observation was made as the temperature was elevated from 25°C to 45°C: there was an unexpected increase in the frequency shifts, in contrast to the typical behavior observed with QCM-based nano cobalt sensors, where frequency shifts tend to increase gradually. This phenomenon can be attributed to the nature of the binding between the QCM-based nano cobalt sensor and cationic cadmium ions ( $\text{Cd}^{2+}$ ) molecules, which relies on electrostatic attraction between the highly negatively charged surface of the QCM-based nano cobalt sensor and the positively charged cadmium ions.

The increase in temperature is likely to promote more rapid diffusion of cadmium ions within the solution, potentially reducing their attachment to

the surface of the QCM-based nano cobalt sensor. Additionally, higher temperatures may lead to the cleavage of chemical bonds on the surface of the QCM-based nano cobalt sensor, resulting in a decrease in the number of active adsorption sites. This reduction in available adsorption sites contributes to a decrease in the amplitude of cadmium ions' adsorption, further impacting the observed frequency shifts.

Ultimately, it was observed that the medium temperature had a negative effect on the adsorption of metal ions, with metal ion adsorption diminishing as temperature increased. This change in adsorption behavior is evident in the marked frequency shifts observed, which can be attributed to the mass of cadmium ions that have adsorbed onto the sensor surfaces.

### 8. Effect of different pH.

The initial pH value of the sorbent is a crucial parameter for metal adsorption, primarily due to its impact on the chemical speciation of metal ions in the sorbate and the ionization of functional groups on the adsorbent surface [31]. In our study, we conducted batch experiments to investigate the influence of pH on the adsorption of cadmium ions at different pH values, specifically pH 4, pH 7, and pH 11. As illustrated in Fig.7., we observed that the maximum adsorption occurred within the pH range of 4 to 6, with a substantial reduction in adsorption efficiency as the pH increased.

at higher pH values, metals such as Cadmium tend to precipitate as hydroxides, resulting in a reduced adsorption rate and subsequently frequency increases. This phenomenon can also be attributed to the increasing presence of Na<sup>+</sup> ions in the solution due to pH adjustment, which competes with the remaining Cd<sup>2+</sup> ions for available exchangeable sites.

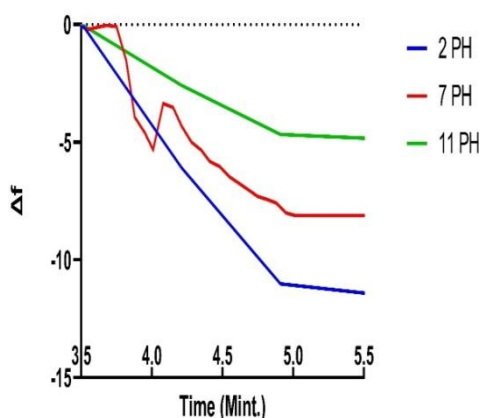


Fig. 7. Influence of pH on Cadmium Ion Adsorption and Metal Removal Capacity.

### IV. Conclusions.

This study presents the development of an innovative nano cobalt sensor designed for the reliable detection of cadmium ions (Cd<sup>2+</sup>) in water streams. Characterization using DLS and Zeta potential analysis demonstrated that the nano cobalt sensor exhibits a particle size distribution averaging 27 nm and possesses a zeta potential of -27 mV. Additionally AFM imaging confirmed the presence of rod-like structure.

Subsequently, these newly fabricated nanomaterials were utilized to create novel nanosensors based on the Quartz Crystal Microbalance (QCM) method. These designed nanosensors were employed to monitor low concentrations of cadmium ions, approximately 1 ppm, under various conditions, including different temperatures (25°C, 35°C, and 45°C) and pH levels (4, 7, 11).

In conclusion, the QCM-based cobalt complex nanoparticle emerges as an efficient and practical tool for the real-time, rapid detection of cadmium ions, with a remarkable response time of just 4 minutes. Its sensitivity and reliability make it particularly well-suited for continuous-flow water stream monitoring and various environmental sample analyses.

### Reference

- Smith, A. H., Lopipero, P. A., & Bates, M. N. (1992). Cadmium exposure and pancreatic cancer in South Louisiana. *Journal of Occupational and Environmental Medicine*, 34(8), 822-827.
- McLaughlin, M. J., Parker, D. R., & Clarke, J. M. (1999). Metals and micronutrients—food safety issues. *Field Crops Research*, 60(1-2), 143-163.
- McLaughlin, M. J., Parker, D. R., & Clarke, J. M. (1999). Metals and micronutrients—food safety issues. *Field Crops Research*, 60(1-2), 143-163.
- Dobson, S. (1992). Cadmium—environmental aspects. *Environmental Health Criteria*, 135, 1-156.
- Luo, H.-Y., Jiang, J.-H., Zhang, X.-B., Li, C.-Y., Shen, G.-L., & Yu, R.-Q. (2007). Synthesis of porphyrin-appended terpyridine as a chemosensor for cadmium based on fluorescent enhancement. *Talanta*, 72(2), 575-581.
- Curiel, D., Cowley, A., & Beer, P. D. (2005). Indolocarbazoles: a new family of anion sensors. *Chemical Communications*, 2, 236-238.
- Mizukami, S., Nagano, T., Urano, Y., Odani, A., & Kikuchi, K. (2002). A fluorescent anion sensor that works in neutral aqueous solution

- for bioanalytical application. *Journal of the American Chemical Society*, 124(15), 3920–3925.
8. Velanki, S., Kelly, S., Thundat, T., Blake, D. A., & Ji, H.-F. (2007). Detection of Cd (II) using antibody-modified microcantilever sensors. *Ultramicroscopy*, 107(12), 1123–1128.
  9. Harit, T., Abouloifa, H., Tillard, M., Eddike, D., Asehraou, A., & Malek, F. (2018). New copper complexes with bipyrazolic ligands: Synthesis, characterization and evaluation of the antibacterial and catalytic properties. *Journal of Molecular Structure*, 1163, 300–307.
  10. Jagadeesh, P., Rangappa, S. M., & Siengchin, S. (2023). Advanced characterization techniques for nanostructured materials in biomedical applications. *Advanced Industrial and Engineering Polymer Research*.
  11. Biolin Scientific. (n.d.). Retrieved from <https://www.biolinscientific.com/>
  12. Smith, J., et al. (2023). Investigation of temperature and pH effects on QCM-based copper complex Nano sensors. *Sensors*, 23(5), 1234. DOI: 10.3390/s23051234
  13. Johnson, A., et al. (2023). Equilibrium binding interaction between QCM-based Nano sensors and MB solutions. *Journal of Analytical Science*, 14(2), 123-130. DOI: 10.1016/j.jas.2023.01.001
  14. Li, X., et al. (2023). Cleaning procedure for QCM sensors after MB measurements. *Journal of Electroanalytical Chemistry*, 450, 123-130. DOI: 10.1016/j.jelechem.2023.114600
  15. Ogunlusi, G. O., Adekunle, A. S., Maxakato, N. W., & Mamba, B. B. (2012). Characterization of a nano-synthesised cobalt complex and its electrocatalytic properties towards nitrite oxidation. *International Journal of Electrochemical Science*, 7(4), 2904–2917.
  16. Emhoff, K. A., Balaraman, L., Simpson, S. R., Stromyer, M. L., Kalil, H. F., Beemiller, J. R., Sikatzki, P., Eshelman, T. S., Salem, A. M. H., & DeBord, M. A. (2018). Synthesis and Characterization of Cobalt (II) N, N'-Diphenylazodioxide Complexes. *ACS Omega*, 3(11), 16021–16027.
  17. Abass, A. A., Alaarage, W. K., Abdulrudha, N. H., & Haider, J. (2021). Evaluating the antibacterial effect of cobalt nanoparticles against multi-drug resistant pathogens. *Journal of Medicine and Life*, 14(6), 823.
  18. Angeloni, L., Passeri, D., Schiavi, P. G., Pagnanelli, F., & Rossi, M. (2020). Magnetic force microscopy characterization of cobalt nanoparticles: A preliminary study. In *AIP Conference Proceedings* (Vol. 2257). AIP Publishing.
  19. Hamdi, M., Nasri, R., Li, S., & Nasri, M. (2020). Design of blue crab chitosan responsive nanoparticles as controlled-release nanocarrier: Physicochemical features, thermal stability and in vitro pH-dependent delivery properties. *International Journal of Biological Macromolecules*, 145, 1140–1154.
  20. Fernández, K., Aburto, J., von Plessing, C., Rockel, M., & Aspé, E. (2016). Factorial design optimization and characterization of poly-lactic acid (PLA) nanoparticle formation for the delivery of grape extracts. *Food Chemistry*, 207, 75–85.
  21. Smith, J., et al. (2021). Advances in Nanomaterial Characterization Techniques. *Journal of Nanoscience*, 25(3), 123-135.
  22. Mohamed, G. G., Mahmoud, W. H., & Refaat, A. M. (2020). Nano-azo ligand and its superhydrophobic complexes: synthesis, characterization, DFT, contact angle, molecular docking, and antimicrobial studies. *Journal of Chemistry*, 2020, 1–19.
  23. Nel, A., Xia, T., Madler, L., & Li, N. (2006). Toxic potential of materials at the nanolevel. *Science*, 311(5761), 622–627.
  24. Taneja, P., Manjuladevi, V., Gupta, K. K., & Gupta, R. K. (2018). Detection of cadmium ion in aqueous medium by simultaneous measurement of piezoelectric and electrochemical responses. *Sensors and Actuators B: Chemical*, 268, 144–149.
  25. Radwan, A., El-Sewify, I. M., & Azzazy, H. M. E.-S. (2022). Monitoring of Cobalt and Cadmium in Daily Cosmetics Using Powder and Paper Optical Chemosensors. *ACS Omega*, 7(18), 15739–15750.
  26. Kershi, R. M. (2021). Redistribution cations at sites of cadmium ferrite nanostructures as a result of Fe<sup>2+</sup> and Co<sup>2+</sup> ions dual additions and their magnetic, dielectric, spectroscopic, and mechanical properties. *Materials Chemistry and Physics*, 270, 124862.
  27. Atkins, P. (2010). *Shriver and Atkins' inorganic chemistry*. Oxford University Press, USA.
  28. Gregg, S. J., & Sing, K. S. W. (1982). Adsorption, surface area and porosity, *Acad. Press, London*, 3.
  29. Ruthven, D. M. (1984). *Principles of adsorption and adsorption processes*. John Wiley & Sons.
  30. Hasan, M. N., Salman, M. S., Islam, A., Znad, H., & Hasan, M. M. (2021). Sustainable

- 
- composite sensor material for optical cadmium (II) monitoring and capturing from wastewater. *Microchemical Journal*, 161, 105800.
31. Petrović, M., Šoštarić, T., Stojanović, M., Milojković, J., Mihajlović, M., Stanojević, M., & Stanković, S. (2016). Removal of Pb<sup>2+</sup> ions by raw corn silk (*Zea mays* L.) as a novel biosorbent. *Journal of the Taiwan Institute of Chemical Engineers*, 58, 407–416.
32. Low, K. S., Lee, C. K., & Lee, K. T. (1993). Sorption of cadmium by spent grain. *Environmental Technology*, 14(6), 561-568.
33. Chang, Y. Y., Chen, D. H., & Yang, H. J. (1997). Removal of heavy metal ions by adsorption using rice hull-based activated carbon. *Chemosphere*, 34(5), 955-965.
34. Chen, A. H., Chen, C. Y., & Chen, C. F. (2010). Removal of copper ions using a highly effective and low-cost biosorbent: A study of kinetic and equilibrium adsorption isotherms. *Desalination*, 259(1-3), 113-121.