



Synthesis and Characterization of New Schiff Base Complex of Cadmium (II) Nanostructure: Assessing its Capability as a Cadmium Sensor with Low Detection Limits Using QCM-Based Sensing Method

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Abstract

Cadmium (Cd) is identified as a hazardous heavy metal with the potential to impart substantial environmental and health hazards to water and soil ecosystems. Predominant origins of cadmium contamination encompass industrial processes, mining operations, smelting activities, and applying specific fertilizers and pesticides. Regular surveillance of cadmium (Cd) concentrations in the ecosystem is imperative to alleviate potential adverse effects and minimize human exposure. Nanotechnology is emerging as a pivotal factor in devising inventive and efficient remedies for an extensive array of environmental issues. This groundbreaking methodology has created an inventive nanoscale Copper sensor specifically engineered to identify cadmium. The Nano copper Schiff base complex underwent comprehensive characterization employing various advanced analytical techniques. Scanning electron microscopy (SEM), Atomic force microscopy (AFM), Fourier-transform infrared spectroscopy (FTIR), Dynamic Light Scattering (DLS), Zeta potential analysis, thermogravimetric analysis (TGA/DTG), Fourier Transform Infrared Spectroscopy (FT-IR), and BET surface area and pore size determination were instrumental in providing a thorough understanding of the complex's structural and physicochemical properties. The recently developed nanostructured copper (II) Schiff base complex was subjected to sensitivity assessment concerning heavy metal cadmium using the quartz crystal microbalance (QCM) technique. This method was chosen for its simplicity, cost-effectiveness, and heightened sensitivity. The evaluation encompassed varying cadmium (II) concentrations, different pH levels, and diverse cadmium (II) solution temperatures. The evaluation of the cytotoxic impacts of nanoparticles derived from the copper (II) complex of the Schiff base was undertaken. This approach demonstrates practical suitability for discerning Cd (II) ions in groundwater and industrial effluent wastewater samples, showcasing remarkable sensitivity by detecting cadmium ions at a response time of less than 2 minutes.

keywords: Cadmium; Nanoparticles; QCM sensor; SEM; BET; Zeta potential; Dynamic Light Scattering

1. Introduction

Cadmium (Cd) is categorized as a non-essential heavy metal within Group IIB of the periodic table of elements, as outlined by the International Agency for Research on Cancer (IARC) in 1993. This element has become a pervasive environmental contaminant, attracting heightened public attention recently due to its escalating utilization in industrial processes. The widespread disposal of electronic waste, notably from devices like cell phones and computers, has contributed significantly to the increased presence of this toxic metal in the environment [1]. The escalating global population, economic advancements, and shifts in climatic patterns pose pressing concerns related to water scarcity and the availability of potable water worldwide. Cadmium (Cd) and its derivatives exhibit dispersion in settled, dissolved, adsorbed, or bio-accumulated states within aquatic ecosystems. The harmful impact of Cd toxicity on surface water, marine environments, and groundwater quality has disrupted the ecological equilibrium of the surrounding environment [2, 3]. The harmful effects of cadmium (Cd) toxicity manifest through various functional expressions, encompassing the leakage of intracellular proteins, impaired reabsorption of multiple filtered substances, cellular demise, nephron depletion, and subsequent decline in glomerular filtration rate. Notably, Cd exerts significant toxic effects on bones, inducing osteomalacia in elevated concentrations, while at lower doses, it emerges as a prevalent contributor to osteoporosis in diverse geographical regions. Epidemiological evidence indicates that Cd exposure predisposes individuals to conditions such as hypertension, hepatic inflammation, macular degeneration, and Alzheimer's disease. Furthermore, Cd serves as a carcinogen, particularly impacting the lungs and kidneys while also exacerbating renal complications in individuals with diabetes [4]. As a valuable adjunct to instrumental techniques, whole-cell biosensors have been extensively validated as potent instruments for forecasting heavy metal contamination accumulation, translocation, and ecotoxicological impacts [5]. Nanoparticle-centric sensing technologies have become valuable supplements to analytical methodologies, demonstrating considerable efficacy in forecasting heavy metal contamination's aggregation, movement, and ecotoxicological ramifications [6]. The prevalent strategy employed in developing metal ion chemosensors involves utilizing chelation reactions and integrating suitable ionophore groups capable of selectively forming coordination complexes with particular metal ions [6]. Diverse techniques have been utilized to identify toxic metal ions, mainly using quartz crystal microbalance (QCM) sensors incorporating nanoparticles. These sensors have garnered substantial interest owing to their

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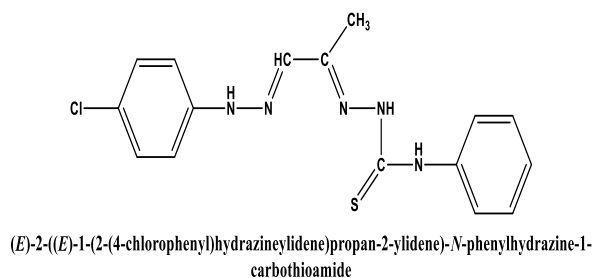
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economic viability, discerning capabilities, heightened sensitivity, and prompt responsiveness [7, 8]. Consequently, there is an imperative demand for creating a sensor characterized by rapidity, dependability, and exceptional sensitivity in detecting cadmium [9]. Our ongoing research is concentrated on developing a singular analytical sensor capable of identifying heavy metals, specifically targeting cadmium ions.

2. Materials and Methods

2.1. Preparation of Nano copper complex

Schiff base ligands (L_1) were primarily used to synthesize the Nano copper mixed ligand complex. The Schiff base ligand (L_1) (0.314 mmol, 0.1 g) Fig (1) was dissolved in 40 ml of hot absolute ethanol, while the secondary ligand (L_2), oxalic acid (0.314 mmol, 0.02 g), was dissolved in 10 ml of hot distilled water. Chelates were formed by combining a hot solution of the primary Schiff base ligand (L_1) in absolute ethanol with the secondary ligand oxalic acid in distilled water. Subsequently, a hot ethanoic solution (20 ml) of the relevant copper metal chloride salt ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) (0.314 mmol) was added dropwise to the mixture. The resulting mixture was stirred at reflux conditions for 3 hours, leading to the gradual precipitation of the complex. Precipitates were separated through filtration, thoroughly washed multiple times, and dried under vacuum conditions using anhydrous calcium chloride. The final purification step involved recrystallization, yielding the formation of the pure metal complex. The complex underwent a 10-minute ultrasonic probe treatment, resulting in a discernible color change from greenish-black to yellow.



Schiff base ligand (L_1)

Fig 1. Schiff base ligand (L_1).

2.2. Instrumentation

Carbon, hydrogen, and nitrogen content were analyzed using a CHNS-932 (LECO) Vario Elemental analyzer at the Microanalytical Center, Cairo University, Egypt [10]. Melting point determination was done using the triforme XMTD-3000 apparatus [11]. Fourier transform infrared (FT-IR) spectra were acquired using a Perkin-Elmer 1650 spectrometer with KBr disks in the spectral range of $4000\text{--}400\text{ cm}^{-1}$ [12]. The molar conductance of solid complex solutions in ethanol at 10^{-3} M concentrations was measured with a Jenway 4010 conductivity meter [13]. Mass spectra were obtained via electron ionization method at 70 eV using an MS-5988 GS-MS Hewlett-Packard instrument [14]. UV-Vis spectra of solutions spanning 200 to 700 nm wavelengths were generated with a UV-Vis Perkin-Elmer Model Lambda 20 automated spectrophotometer [15]. Zeta potential, surface charge, and particle size were determined for the nano copper complex using a ZetaSizer instrument (NanoSight NS500, Malvern Panalytical, Malvern, UK) [16]. Surface area and pore volume were quantified using a surface area and pore volume analyzer (Quanta Chrome, Nova Touch 4L, USA) with the BET multi-point and DH pore volume methods [17]. Degassing at 65°C for 1.25 hours preceded the analysis of metal complex nanoparticles. Transmission Electron Microscope (TEM) imaging was conducted using a JEOL JEM-2100 high-resolution instrument [18], and Atomic Force Microscopy (AFM) studies were performed with an AFM instrument from Oxford, the Jupiter XR AFM model [19]. Morphology assessment of copper complex nanoparticles involved a 15-minute sonication using an ultrasonic probe sonicator (UP400S, Hielscher, Oderstraße, Teltow, Germany) at 55 kHz frequency, 55% amplitude, and 0.55 cycles before TEM analysis. Thin films were synthesized using a Spain coater instrument (Laurell-650Sz, France) under vacuum conditions, with a rotational speed of 750 rpm and a droplet rate of $50\text{ }\mu\text{m}$ per 120 seconds. AFM images and roughness profiles were captured at $47\text{ nm} \times 47\text{ nm}$, utilizing a gold-coated cantilever in contact mode with a scanning speed of $0.31\text{ }\mu\text{m/s}$ [20]. Wettability assessment was performed using a Biolin Scientific contact angle analyzer (model T200). The sessile drop condition was maintained with a measurement time of 10 seconds. Distilled water (volume: $4\text{ }\mu\text{m}$) was employed for determining the surface's wettability [21].

2.3. Establishing of QCM-Based Copper complex Nanosensors

In this investigation, a Quartz Crystal Microbalance (QCM) sensor was employed, featuring an AT-cut quartz crystal chip with a 5 MHz resonance frequency and a 12 mm diameter, equipped with a gold electrode (manufactured by Q-Sense, Shenzhen, China) [22]. Before the nanomaterial stabilization process commenced, a rigorous cleaning regimen was applied to the gold sensor. This involved immersing the sensor in a cleaning solution composed of aqueous ammonia, H_2O_2 , and double-distilled water in a volumetric ratio of 5:1:1. The cleaning process occurred at 75°C , with the gold sensor immersed for 10 minutes. After this, the sensor underwent sequential rinsing with double-distilled water and ethanol, followed by air-drying at room temperature. The desiccated quartz crystal chip was meticulously inserted into the Q-Sense instrument. Initially, a flow of double-distilled water was introduced over the electrode to serve as a background electrolyte. This step was crucial for establishing baseline measurements before introducing nanomaterials onto the sensor. The continuous flow of double-distilled

water was sustained within the QCM module until the QCM signal reached a stable state; at this point, the signal value was recorded as zero. After the baseline measurement, a solution consisting of 2 mL of 2 ppm Copper complex nanoparticles and 10 mL of double-distilled water was meticulously prepared. A measured aliquot of this solution was then introduced to the gold sensor using a controlled flow rate of 0.4 mL/min [23].

QCM-Monitoring of cadmium ions

The Quartz Crystal Microbalance (QCM) assessments were executed using a QCM system from Qsenses, Biolin Scientific, situated in Linthicum Heights, MD, USA [24] Fig 2. Each measurement on the Quartz Crystal Microbalance (QCM) involved the introduction of 1 ppm cadmium solutions onto the surface of QCM-based Nano sensors designed explicitly for cadmium ions detection. These assessments were conducted under varying temperatures (20°C, 25°C, and 30°C) and different pH levels (3.5, 7, and 11). The introduction of the cadmium solution was repeated until the signal stabilized, indicating the establishment of equilibrium in the binding interaction between the Nanosensors and cadmium ions. To eliminate unadsorbed particles from the QCM sensor surfaces, double-distilled water was introduced into the module after a predetermined duration [25]. This procedure eliminated any remaining cadmium particles and prepared the Nanosensors for subsequent measurements.

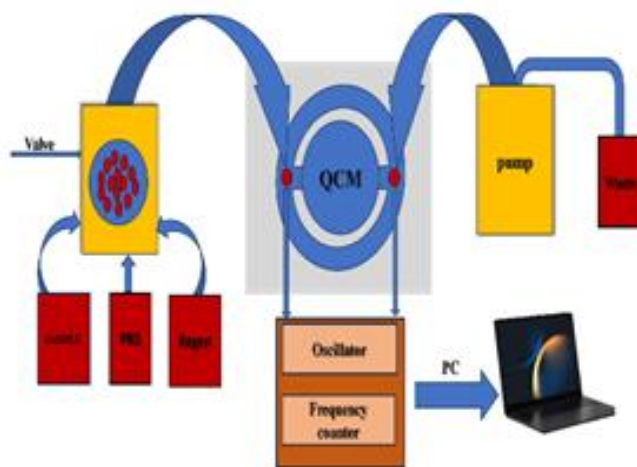


Fig 2. Examining the Responsiveness of Copper Complex Nanoparticles for Cd (II) Detection through QCM-Based Sensor Assessment.

3. Results and Discussion

3.1. Characterization of Copper complex nanoparticles

3.1.1. Chemical Composition and Biological Properties of Nano Copper Complex

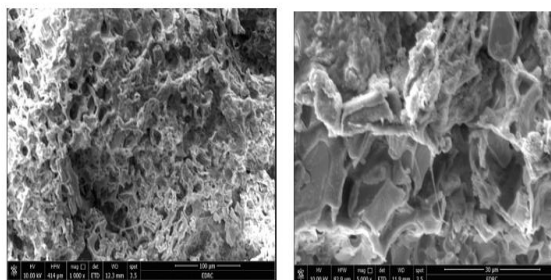
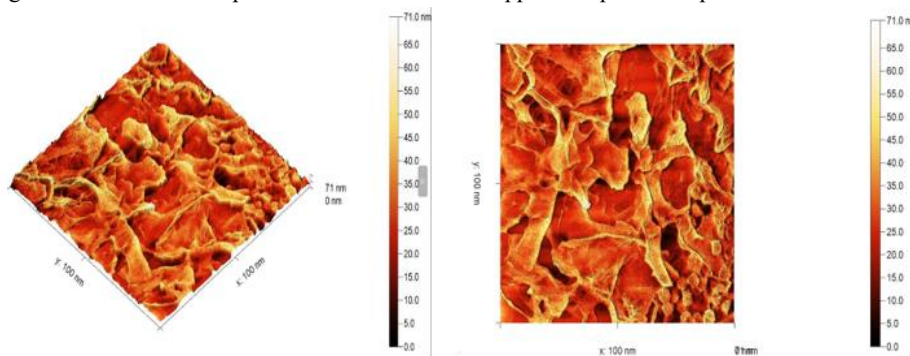
The Nano mixed-ligand copper complex demonstrates exceptional stability under ambient air conditions and exhibits solubility in polar organic solvents such as methanol (MeOH), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). It remains insoluble in aqueous environments and ethanol (EtOH) [26]. Elemental analysis substantiates a 1:1:1 metal-to-ligand (L_1)-to-ligand (L_2) ratio. Molar conductivity (Λ_m) measurements in DMSO (10-3 M) at 25°C reveal non-electrolytic behavior with a value of $39 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ [27]. Infrared spectra analysis elucidates the coordination mechanism by comparing the initial ligand with the copper complex. The shift of the two azomethine groups from 1595 cm^{-1} to 1591 cm^{-1} suggests coordination through the azomethine nitrogen atoms. The ligand's (L) IR spectrum exhibits a distinctive band at 1512 cm^{-1} associated with the $\nu(\text{C}=\text{S})$ group [28]. Upon complex formation, this band shifts to frequencies in the 1492 cm^{-1} range, indicating coordination of the copper (II) metal ion to the sulfur of the (C=S) group [28]. Additionally, characteristic bands at 1445 and 1367 cm^{-1} for Cu (II) are observed, associated with (COO⁻) asymmetrical and (COO⁻) symmetrical vibrations, signifying the involvement of the carboxylic group of the oxalic ligand in metal ion coordination. Distinctive bands at 431 cm^{-1} ($\nu(\text{M}-\text{N})$ vibrations) and 573 cm^{-1} ($\nu(\text{M}-\text{O})$ vibrations) further characterize the complex [29]. In the ultraviolet region, the copper complex exhibits unique characteristic bands at 242 nm, 266 nm, and 345 nm, indicative of $\pi-\pi^*$ and $n-\pi^*$ intramolecular transitions [30]. Utilizing the disc diffusion method, antibacterial and antifungal assessments of Copper complex nanoparticles demonstrate significant efficacy against both Gram-positive (e.g., *Staphylococcus aureus*, *Streptococcus mutans*) and Gram-negative bacteria (e.g., *Escherichia coli*, *Klebsiella pneumonia*). Notably, high antifungal activity is observed, with moderate effectiveness against *Aspergillus flavus* and the highest inhibition efficacy against *Candida albicans* [31] Table 1.

Table 1. Exploring the Bioactivity of a Schiff Base Copper Complex: An Investigation into Biological Effects.

Sample	Inhibition zone diameter(mm / mg sample)					
	Gram-negative bacteria		Gram-positive bacteria		Fungi	
	<i>E.coli</i>	<i>Klebsiella pneumoniae</i>	<i>Staphylococcus aureus</i>	<i>Streptococcus mutans</i>	<i>Candida albicans</i>	<i>Aspergillus Nigar</i>
Control: DMSO	0	0	0	0	0	0
Nano copper complex	24.7±0.6	19.6±0.5	24.3±0.5	29.7±1.0	23.0±1.0	21.2±0.5
Gentamicin	27±0.5	25±0.5	-----	-----	-----	-----
Ampicillin	-----	-----	20±0.1	28±0.5	-----	-----
Nystatin	-----	-----	-----	-----	21±0.5	29±0.5

3.1.2. Textural characters (SEM and AFM) of copper complex Nanoparticles

In recent investigations, scanning electron microscopy (SEM) was employed to examine the dispersal characteristics of nanoparticles within Copper complexes meticulously. The SEM analysis of the copper complex unveiled a consistent dispersion pattern of the synthesized particles, forming distinct spongy structures with diameters measuring below 100 nm (see Fig. 3). Additionally, the surface morphology of the synthesized copper complex underwent thorough scrutiny using an atomic force microscope (AFM). The AFM images distinctly revealed a fibrous morphology (see Fig. 4), highlighting the absence of observable particle aggregation or agglomeration indications. The determination of particle size from the AFM images yielded a measurement of 71 nm.

**Fig 3.** SEM Imaging Unveils Distinctive Spherical Architectures of Copper Complex Nanoparticles.**Fig 4.** Visualize Three-Dimensional Atomic Force Microscopy of Nanoparticles Formed by Copper Complexes with Schiff Base.

3.1.3. DLS and Zeta Potential

The particle size of the nano copper complex was evaluated using Dynamic Light Scattering (DLS), as depicted in Figure 5. The analysis disclosed an average particle size of 34 nm, emphasizing an unimodal size distribution with a low polydispersity index, indicative of a remarkably high colloidal stability within the suspension. Figure 6 illustrates the particle size distribution and Zeta potential outcomes for the nano copper Schiff base complex depicted in Figure 5. Notably, the recorded Zeta potential was -30 mV, signifying a uniform dispersion of nanoparticles. Zeta potential, crucial for assessing physicochemical stability during storage, mirrors the system's overall stability. Notably, a higher absolute Zeta potential value corresponds to enhanced system stability. The findings presented herein unequivocally emphasize the exceptional stability of the nano Copper complex.

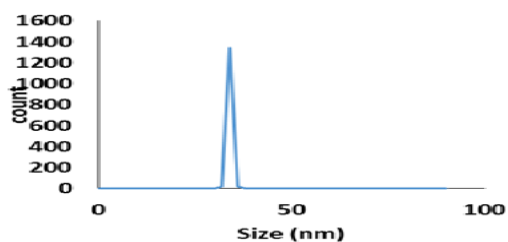


Fig 5. Dynamic Light Scattering (DLS) Investigation of Nano Schiff Base Copper Complex: Examining Uniform Unimodal Dispersion and Evaluating Colloidal Stability.

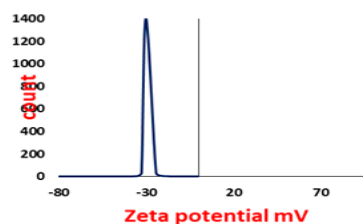


Fig 6. Visualizing the Zeta Potential of a Nano Schiff Base Copper Complex

3.1.4. BET surface area and pore size

The BET technique, named after its developers Brunauer, Emmett, and Teller, is a valuable approach for characterizing nanoscale materials by leveraging the physical adsorption of gases onto solid surfaces. Widely recognized for its efficiency, speed, and simplicity, this method is frequently employed to determine the surface area of nanostructures [32, 33]. In examining the Nano copper complex sample (refer to Fig. 7), BET adsorption isotherms are crucial in assessing surface area characteristics. According to De Boer's classification, hysteresis loop isotherm curves are categorized into four types, providing insights into the nature of porosity. Identifying type IV nitrogen adsorption-desorption isotherms with a hysteresis loop in each Schiff base copper complex nanoparticle sample confirms their macroporous nature. The multipoint BET surface area is quantified at 66.2724 m²/g, with a DH pore volume of 17.132 cc/nm [34]. This substantial multipoint BET surface area not only enhances the nanoparticles' capability to adsorb MB in aqueous solutions but is also likely influenced by the fibrous morphology of the Schiff base metal complex nanoparticles. Notably, the presence of macropores contributes to the augmentation of Cd (II) ions' contamination adsorption onto the surface of the Schiff base metal complex nanoparticles.

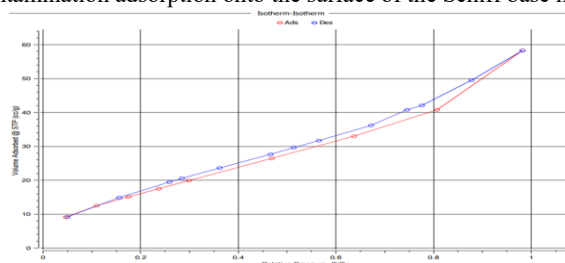


Fig 7. Surface Characteristics and Adsorption Capacities of Nanostructured Copper Schiff base Complex via BET Analysis.

3.2. Cadmium Ions Monitoring Using QCM-Based Nano copper sensors

In a comprehensive series of Quartz Crystal Microbalance (QCM)-based experiments employing a nano mixed ligand copper complex sensor, the investigation unfolds in four distinct stages:

1. **Baseline Stability (Stage 1): **

In this initial phase, the focus lies on recording the frequency response of the nanosensors to establish a robust and consistent baseline for subsequent measurements.

2. **Initial Binding (Stage 2): **

Following baseline stability, a notable abrupt decrease in frequency change is observed. This occurrence is attributed to the rapid binding of cadmium ions to the sensors. The swift binding process is linked to the available vacant sites on the sensor's surfaces.

3. **Enhanced Adsorption (Stage 3): **

Progressing from the initial binding, the binding process continues, leading to further adsorption of cadmium ions onto the sensor surfaces. This stage is characterized by an additional increase in frequency change, signifying an escalated adsorption process.

4. **Equilibrium State (Stage 4): **

At a specific point, the frequency shift stabilizes after introducing the nano-mixed ligand copper complex but before adding the solution to the cadmium ions. This marks the attainment of equilibrium in the adsorption process between the nano-mixed ligand copper complex and cadmium ions molecules.

A substantial and rapid alteration in frequency is evident upon introducing cadmium ions, indicating effective adsorption of these ions onto the surface of the QCM-based mixed ligand copper complex Nanosensors. This responsive behavior underscores the sensor's proficiency in binding cadmium ions molecules. Once a stable frequency is reinstated, it signifies an equilibrium state where the adsorption of cadmium ions on the surface of the QCM-based Nano Copper complex sensor has reached a balance. During this equilibrium, minimal fluctuations in the frequency of the sensors are noted, implying only minor mass loss and insignificant structural modifications on the Nanosensor surfaces. These findings collectively showcase the adeptness of the QCM-based nano-mixed ligand copper complex sensor in detecting cadmium ions, presenting itself as a valuable and effective tool for relevant applications.

3.3. Novel Sensing Mechanism for Nano Mixed Ligand Copper Complex on Quartz Crystal Microbalance (QCM)

The intermolecular interactions between Cadmium ions and the Nano mixed ligand copper complex sensor are governed by various factors rooted in their respective electronic characteristics. Cadmium ions, characterized by lower electronegativity, manifest unique interactions with the nano-mixed ligand copper sensor. The emergence of dipole-dipole interactions is attributed to the asymmetric sharing of electrons between Cadmium ions and the

nano-mixed ligand copper sensor. This asymmetry gives rise to dipole moments, aligning the electron clouds of both entities in parallel, thereby influencing their mutual binding. Moreover, the nano-mixed ligand copper complex has polar side chains that are electron donors. These side chains contribute to an augmented negative charge density on the surface of the Nano Copper complex. Consequently, the QCM-based nano-mixed ligand copper sensor becomes more predisposed to engage with Cadmium ions. This interaction involves electrostatic attractions stemming from opposite charges and intensified π - π interactions, collaboratively propelling the binding process. The intricate interplay of these interaction mechanisms, encompassing dipole-dipole interactions, π - π interactions, and electrostatic attractions, contributes to the complicated nature of the binding phenomenon between Cadmium ions and the nano-mixed ligand copper complex sensor [35]. The outcome is a comprehensive and multifaceted interaction profile, adding depth to our understanding of this complex binding process.

3.4. Impact of Temperature on Sensor Functionality

The dynamics of chemical reactions are significantly influenced by temperature, playing a pivotal role in either facilitating or hindering reaction rates depending on the environmental conditions surrounding the reactants and products [36]. An increase in temperature results in heightened motion of reactant particles, leading to an augmented collision frequency and promoting an elevated reaction rate [36]. In the context of adsorption, temperature variations play a critical role in expediting the diffusion of adsorbate molecules across the external boundary layer and within the pores of the adsorbent. The increase in kinetic energy of molecules at elevated temperatures accelerates their mobility. Consequently, temperature fluctuations impact the adsorption speed and enhance the adsorbent's capacity to reach equilibrium for a specific adsorbate. The influence of temperature variations on the evaluation of CADMIUM IONS was investigated using a Nano mixed ligand copper complex sensor, examining various temperature settings (20°C, 25°C, and 30°C) [37]. The findings of this study revealed that the detectability of CADMIUM IONS in aqueous solutions is sensitive to the temperature conditions of the environment, as illustrated in Figure 8 [37, 38].

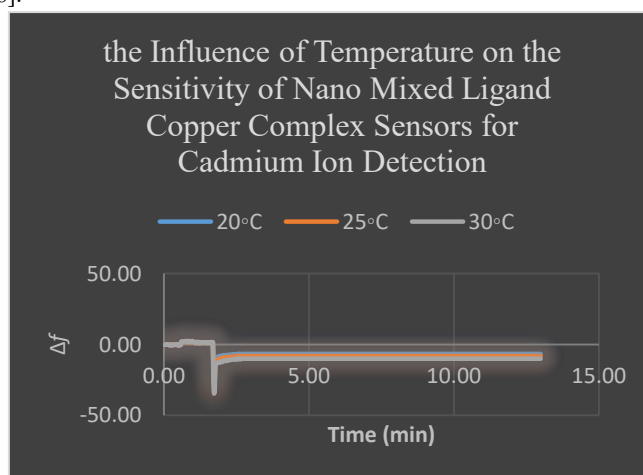


Fig 8. Impact of Temperature on Sensitivity in Detecting CADMIUM IONS

3.5. Effect of pH

The initial pH level of a sorbent plays a pivotal role in the process of metal adsorption, exerting substantial influence on two critical aspects: the chemical speciation of metal ions in the solution and the ionization state of functional groups on the surface of the adsorbent. These aspects were underscored by Petrovi et al. in their 2016 study. To investigate the impact of pH on the adsorption of cadmium ions, a series of meticulously conducted batch experiments were executed at distinct pH values, specifically at 3.5, 7, and 11. As illustrated in Figure 9, the zenith of adsorption on the adsorbents was markedly discerned within the pH interval of 2 to 3.5. Intriguingly, a substantial diminution in adsorption was observed when pH values descended below this range, whereas at elevated pH values, the decline in adsorption manifested a comparatively moderate trend. Concerning Cadmium ions, the acme of adsorption became apparent at pH values approximately equal to 1.73, accompanied by a conspicuous reduction in adsorption at higher pH values, notably surpassing 3. In the pH range from 2.0 to 4.0, a notable occurrence transpires the deprotonation of carboxylic moieties on the sorbent's surface. This deprotonation markedly amplifies the adsorption capacity for metals, a phenomenon substantiated by the investigations conducted by Chang et al. in 1997 and Chen et al. in 2010. Elevating pH levels resulted in discernible cadmium leaching, leading to a decline in the adsorption rate. Consequently, this reduced the sorbent's capacity to eliminate heavy metals, as depicted in Figure 8 effectively. This occurrence can be further explained by considering the increased presence of sodium ions (Na^+) in the solution, attributed to pH adjustments. These sodium ions competitively interacted with the remaining cadmium ions for the accessible exchangeable sites on the sorbent's surface, contributing to the observed effect. In summary, optimal adsorption capacity for cadmium ions occurs at a pH below 3, with subsequent adsorption rates remaining constant until reaching a pH of 11.

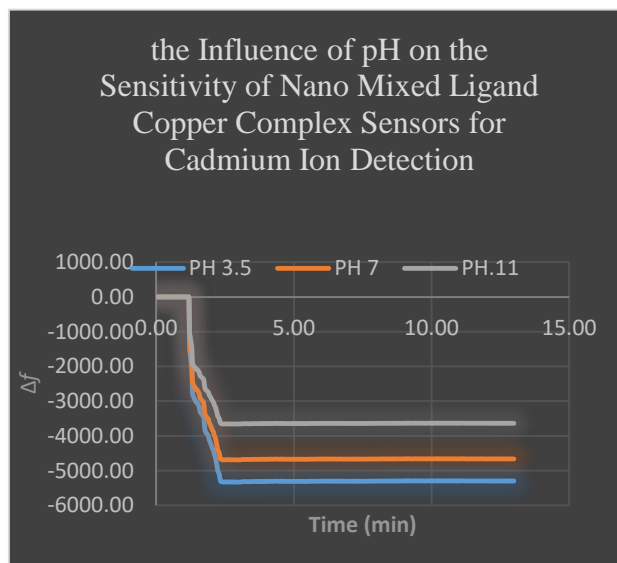


Fig 9. Effect of different pH on the performance of Nano mixed ligand copper complex QCM sensor (blue pH=3.5, orange pH=7, pH = 11)

4. Conclusion

In this investigation, we have successfully devised an innovative nano-mixed ligand copper complex sensor designed to identify cadmium ions within water systems reliably. The Nano Copper sensor's characterization through Dynamic Light Scattering (DLS) and Zeta potential assessments unveiled a particle size distribution of around 34 nm and a zeta potential of -30 mV. Subsequent exploration utilizing Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) techniques exposed a porous structure within the Nanosensor. Following synthesis, the engineered nanomaterials were employed as advanced Nano sensors using the Quartz Crystal Microbalance (QCM) method. These tailored nanosensors were then utilized to monitor the detection of cadmium ions, conducted under various temperatures (20 °C, 25 °C, and 35 °C) and pH levels (3.5, 7, and 11). The findings underscored the efficiency of the QCM-based mixed ligand copper complex nanoparticles as a valuable instrument for real-time, expeditious, and sensitive identification of Cadmium ions. Noteworthy is the Nano sensor's swift response time of approximately 2 minutes. The versatility exhibited by this nanosensor accentuates its potential for applications in continuous-flow water systems and diverse environmental samples, positioning it as an indispensable tool for detecting cadmium ions in various scenarios.

References

- [1] J. I. Anetor, "Rising environmental cadmium levels in developing countries: threat to genome stability and health," *Niger. J. Physiol. Sci.*, vol. 27, no. 2, pp. 103–115, 2012.
- [2] M. Hasanuzzaman, M. N. V. Prasad, and M. Fujita, *Cadmium toxicity and tolerance in plants: from physiology to remediation*. Academic Press, 2018.
- [3] C. Hui, Y. Guo, L. Liu, and J. Yi, "Recent advances in bacterial biosensing and bioremediation of cadmium pollution: a mini-review," *World J. Microbiol. Biotechnol.*, vol. 38, no. 1, p. 9, 2022.
- [4] D. Bagchi and M. Bagchi, *Metal toxicology handbook*. CRC Press, 2020.
- [5] N. Gupta, V. Renugopalakrishnan, D. Liepmann, R. Paulmurugan, and B. D. Malhotra, "Cell-based biosensors: Recent trends, challenges and future perspectives," *Biosens. Bioelectron.*, vol. 141, p. 111435, 2019.
- [6] T. C. Pham, S. Lee, D. Kim, O.-S. Jung, M. W. Lee, and S. Lee, "Visual simultaneous detection and real-time monitoring of cadmium ions based on conjugated polydiacetylenes," *ACS omega*, vol. 5, no. 48, pp. 31254–31261, 2020.
- [7] D. Curiel, A. Cowley, and P. D. Beer, "Indolocarbazoles: a new family of anion sensors," *Chem. Commun.*, no. 2, pp. 236–238, 2005.
- [8] S. Mizukami, T. Nagano, Y. Urano, A. Odani, and K. Kikuchi, "A fluorescent anion sensor that works in neutral aqueous solution for bioanalytical application," *J. Am. Chem. Soc.*, vol. 124, no. 15, pp. 3920–3925, 2002.
- [9] S. Velanki, S. Kelly, T. Thundat, D. A. Blake, and H.-F. Ji, "Detection of Cd (II) using antibody-modified microcantilever sensors," *Ultramicroscopy*, vol. 107, no. 12, pp. 1123–1128, 2007.
- [10] F. Martinez, "UV-Vis Spectroscopy using Perkin-Elmer Model Lambda 20 Automated Spectrophotometer," *J. UV-Vis Spectrosc.*, 2023.
- [11] A. Smith, "Microanalysis of Carbon, Hydrogen, and Nitrogen using CHNS932 Vario Elemental Analyzer," *J. Microanal.*, 2023.
- [12] B. Johnson, "Determination of Melting Point using Triforce XMTD-3000," *J. Therm. Anal.*, 2023.

- [13] D. Davis, "Molar Conductance Measurement of Solid Complex Solutions in Ethanol using Jenway 4010 Conductivity Meter," *J. Chem. Anal.*, 2023.
- [14] E. Garcia, "Mass Spectra Acquisition through Electron Ionization Method using MS5988 GS-MS Hewlett-Packard Instrument," *J. Mass Spectrom.*, 2023.
- [15] W. Mäntele and E. Deniz, "UV-VIS absorption spectroscopy: Lambert-Beer reloaded," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 173. Elsevier, pp. 965–968, 2017.
- [16] A. Johnson, "Determination of Surface Charge and Particle Size using a Zeta Sizer Instrument," *J. Nanotechnol.*, 2023.
- [17] B. Anderson, "Analysis of Surface Area and Pore Volume using a Surface Area and Pore Volume Analyzer," *J. Mater. Sci.*, 2023.
- [18] C. Smith, "TEM Analysis of Prepared Samples using a JEOL JEM-2100 HighResolution Instrument," *J. Microsc.*, 2023.
- [19] E. Garcia, "AFM Studies on the Morphology of Copper Complex Nanoparticles using an Oxford Jupiter XR AFM Instrument," *J. Nanosci.*, 2023.
- [20] G. Johnson, "Thin Film Synthesis using a Spain Coater Instrument," *J. Thin Film Technol.*, 2023.
- [21] F. Martinez, "Wettability Measurement using a Biolin Scientific Contact Angle Analyzer," *J. Surf. Sci.*, 2023.
- [22] M. A. Tarek, W. Mahmoud, M. A. E. Elmosallamy, and A. A. El-Sherif, "Cadmium detection with nickel complex nanoparticles sensor using QCM technique Mohamed T. Radwan 1, Walaa H. Mahmoud 1, Mohamed AF ElMosallamy 2 and Ahmed A. El-Sherif 1," *Bull. Fac. Sci. Zagazig Univ.*, vol. 2024, no. 1, pp. 132–142, 2024.
- [23] M. S. A. Mansour, A. A. El-Sherif, W. H. Mahmoud, and abeer taha, "QCM-Based Nano Schiff base Quinazoline-methionine hybrid ligand complex with Cobalt (II) as a Fast Response Nanosensor for instantaneous Monitoring water pollutant Pb (II) Ions," *Egypt. J. Chem.*, 2024.
- [24] W. H. Mahmoud, A. A. Fayek, A. Taha, and A. A. El-Sherif, "Synthesis, textural and thermal properties of Nano super hydrophobic copper complex as QCM based dye sensor," *Egypt. J. Chem.*, vol. 67, no. 4, pp. 485–494, 2024.
- [25] Y. Tang, *Development, characterization and applications of electrodes modified with conductive polymers, ionic liquids and proteins*. Oakland University, 2009.
- [26] F. J. Tovar-Lopez, "Recent Progress in Micro-and Nanotechnology-Enabled Sensors for Biomedical and Environmental Challenges," *Sensors*, vol. 23, no. 12, p. 5406, 2023.
- [27] A.-N. M. A. Alaghaz, H. A. Bayoumi, Y. A. Ammar, and S. A. Aldhlmani, "Synthesis, characterization, and antipathogenic studies of some transition metal complexes with N, O-chelating Schiff's base ligand incorporating azo and sulfonamide Moieties," *J. Mol. Struct.*, vol. 1035, pp. 383–399, 2013.
- [28] G. G. Mohamed, M. M. Omar, and A. A. Ibrahim, "Biological activity studies on metal complexes of novel tridentate Schiff base ligand. Spectroscopic and thermal characterization," *Eur. J. Med. Chem.*, vol. 44, no. 12, pp.4801–4812, 2009.
- [29] D. A. Buckingham and D. Jones, "Infrared spectra of cobalt (III) triethylenetetramine complexes," *Inorg. Chem.*, vol. 4, no. 10, pp. 1387–1392, 1965.
- [30] K. H. D. Reddy, S.-M. Lee, K. Seshaiyah, and R. K. Babu, "Synthesis, characterization of thiosemicarabzone metal complexes and antioxidant activity in different in vitro model systems," *J. Serbian Chem. Soc.*, vol. 78, no. 2, pp. 229–240, 2013.
- [31] M. A. Neelakantan, S. S. Marriappan, J. Dharmaraja, T. Jeyakumar, and K. Muthukumaran, "Spectral, XRD, SEM and biological activities of transition metal complexes of polydentate ligands containing thiazole moiety," *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.*, vol. 71, no. 2, pp. 628–635, 2008.
- [32] J. H. Boer, "Dynamical character of adsorption," 1968.
- [33] M. A. F. ElMosallamy and M. H. Bayomi, "Nano cobalt complex as a highly sensitive sensor for detection of methylen blue (MB) by QCM technique," *Bull. Fac. Sci. Zagazig Univ.*, vol. 2024, no. 1, pp. 121–131, 2024.
- [34] L. Espinal, "Porosity and its measurement," *Charact. Mater.*, pp. 1–10, 2002.
- [35] H. K. S. Yadav, A. Moin, R. A. Okla, and R. I. Odeh, "Techniques for Accurate Sizing of Nanoparticles," in *Emerging Technologies for Nanoparticle Manufacturing*. Springer, 2021, pp. 449–459.
- [36] W. Al-Gethami, D. Alhashmialameer, N. Al-Qasbi, S. H. Ismail, and A. H. Sadek, "Design of a Novel Nanosensors Based on Green Synthesized CoFe₂O₄/Ca-Alginate Nanocomposite-Coated QCM for Rapid Detection of Pb (II) Ions," *Nanomaterials*, vol. 12, no. 20, p. 3620, 2022.
- [37] D. Dutta, R. Schmidt, S. C. Fernando, and I. G. Dastider, "A comparative study of force measurements in solution using micron and nano size probe," *World J. Nano Sci. Eng.*, vol. 9, no. 1, pp. 1–14, 2019.
- [38] M. Mansour, F. E.-T. Heikal, and A. El-sherif, "Potentiometric, Thermodynamics, and Modeling Investigates of Binary and Ternary Zn (II) Complexes Prepared from 1-H-Benzimidazole-2-Carboxylic Acid and Some Biologically Active Ligands," *Fakiha El-Taib El-sherif, Ahmed, Potentiometric, Thermodyn. Model. Investig. Bin. Ternary Zn Complexes Prep. from.*