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Investigation of Nanostructure of Schiff Base Copper (II) Complex: Synthesis, Characterization, Textural, and Thermal Property Analysis for Evaluating their Effectiveness as Cadmium Sensors with QCM-Based Sensing Method

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Abstract

Instances of cadmium poisoning have been documented across various regions worldwide, presenting a significant global health concern with the potential to impact multiple organs and, in severe cases, result in fatalities on an annual basis. Prolonged exposure to cadmium, whether through inhalation of air, consumption of contaminated water and food, or contact with polluted soil, is associated with carcinogenic effects and systemic toxicity affecting various organ systems. These include but are not limited to the skeletal, urinary, reproductive, cardiovascular, central and peripheral nervous, and respiratory systems. Nano sensors designed for Cd detection leverage the unique properties of nanomaterials, such as quantum dots, nanotubes, and nanoparticles, to enhance sensitivity and selectivity. These nanoscale devices not only offer improved detection limits but also provide the potential for real-time, on-site monitoring, overcoming the limitations of traditional analytical methods. This pioneering approach has resulted in the development of an innovative nanoscale copper sensor designed specifically for the detection and identification of cadmium. The comprehensive characterization of the nano copper Schiff base complex involved a systematic application of advanced analytical methodologies. Techniques such as scanning electron microscopy (SEM), atomic force microscopy (AFM), Fourier-transform infrared spectroscopy (FTIR), dynamic light scattering (DLS), zeta potential analysis, thermogravimetric analysis (TGA/DTG), and BET surface area and pore size determination were employed to elucidate the intricate structural and physicochemical attributes of the complex. Moreover, the utilization of a nano Schiff base copper complex has been employed as an economical, straightforward, and remarkably sensitive sensing platform using Quartz Crystal Microbalance (QCM) technology for the swift identification of cadmium. This Nano Schiff base copper complex sensor exhibits a notable capability to detect cadmium ions at extremely low concentrations, reaching levels as minimal as 1 ppm. It is imperative to highlight that a comprehensive evaluation of the cytotoxicity of the cadmium complex nanoparticles has been conducted to ensure their biocompatibility and safety.

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

Introduction

The origins of cadmium pollution have transformed in tandem with the substantial surge in cadmium utilization during the twentieth century. Cadmium finds widespread application in diverse industrial processes, playing a pivotal role in battery manufacturing, alloy formulation, pigment synthesis, and the fabrication of electroplating materials. Additionally, it is frequently encountered in the production of fertilizers derived from phosphate minerals and the treatment of sewage sludge. Cadmium contamination in soil and the surrounding environment primarily stems from Cd-Ni batteries, municipal waste, and landfills [1]. The ubiquitous presence of cadmium (Cd) contamination in terrestrial and aquatic ecosystems is a global phenomenon that has been consistently documented across various geographical locations [2]. It endures within the ecosystem and exerts various toxicological repercussions on both plant and animal life. Inhalation of cadmium (Cd) in airborne environments, such as those arising from soldering or welding fumes, can result in acute poisoning and

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induce chemical pneumonitis [3]. Beyond their immediate ecological effects, these metal elements exhibit non-degradability and have the potential to accrue within diverse organisms. Elements possessing toxic attributes can undergo electron loss, transitioning into cations [4]. This capability to manifest variable oxidation states empowers their interaction with biological organs. Persistent exposure can result in chronic obstructive pulmonary disease and the development of lung malignancies. The primary hazards associated with prolonged cadmium (Cd) exposure via inhalation or ingestion pertain to renal tubular dysfunction, subsequently leading to disruptions in calcium metabolism and consequential bone degeneration. This may manifest as conditions such as osteoporosis and osteomalacia [5]. Methods for detecting elevated levels of heavy metals may not be universally accessible across all laboratory facilities. Therefore, there is an urgent need to know the amount of pollution and exposure to these heavy metals, and here comes the role of nanomaterials as a cheap and available detector. Nanoparticle-based sensing systems have demonstrated their effectiveness as valuable supplements to analytical techniques, offering robust tools for predicting the accumulation, migration, and ecotoxicological consequences of heavy metal contamination [6]. Among the diverse methods employed for the identification of toxic metal ions, the Quartz Crystal Microbalance (QCM) sensor utilizing nanoparticles has garnered considerable attention. This is due to its cost-effectiveness, selectivity, sensitivity, and rapid response time [7, 8]. There is an immediate need for a rapid, reliable, and highly sensitive sensor specifically designed for the detection of cadmium [9]. Our ongoing scientific inquiry is focused on the development of an advanced analytical sensor designed for the proficient identification of heavy metals, with a specific emphasis on targeting cadmium ions. It is imperative to establish a sensor that exhibits rapid response, unwavering reliability, and heightened sensitivity for the precise detection of cadmium.

Materials and methods

Preparation of Nano Copper Complex

The synthesis of the nano copper complex followed a systematic protocol. Initially, a heated ethanoic solution was prepared at 70°C, incorporating a Schiff base ligand as depicted in Figure 1 (0.842 mmol, 0.240 g). In a separate solution of absolute ethanol (20 ml), heated concurrently, the metal salt (0.842 mmol, 0.2 g $CuCl_2.2H_2O$) was dissolved. After three hours of continuous stirring under reflux conditions, the resulting complex precipitated from the solution. After precipitation, the obtained solids were collected through filtration, subjected to thorough washing, and finally desiccated under vacuum conditions using anhydrous calcium chloride. The purification process was concluded with a recrystallization step. Notably, an intriguing transformation occurred during this procedure, leading to a change in the complex's color from a faint yellow to a deep green. Additionally, the synthesized complex underwent ultrasonic probe treatment for a duration of 10 minutes [10, 11].

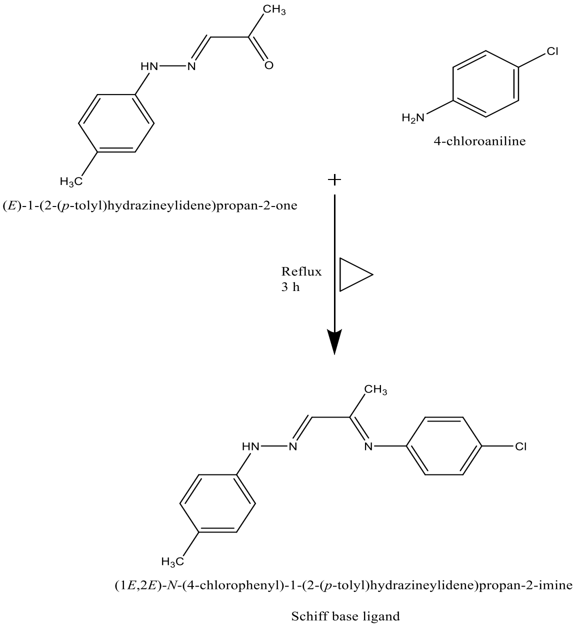


Figure 1. Schiff base ligand **(L)**

Instrumentation.

The investigation conducted at Cairo University in Egypt employed a variety of scientific methodologies and tools for the analysis and characterization of materials, with a focus on exploring their intrinsic properties. The study utilized an array of scientific instruments and techniques to acquire a comprehensive understanding of the composition and distinctive features of the investigated materials. The elemental analysis was performed employing a CHNS-932 (LECO) Vario Elemental analyzer at the Microanalytical Center of Cairo University [12]. This investigation specifically aimed to ascertain the carbon, hydrogen, and nitrogen content in the specimens. The determination of the materials' melting point was executed using a triforce XMTD-3000 apparatus [13]. Fourier transform infrared (FT-IR) spectra were acquired using a Perkin-Elmer 1650 spectrometer with KBr disks, encompassing a spectral range from 4000 to 400 cm^{-1} [14]. To assess the molar conductance of solid complex solutions in ethanol at a concentration of 10^{-3} M, a Jenway 4010 conductivity meter was employed [15]. Mass spectra were acquired through the utilization of an MS-5988 GS-MS instrument manufactured by Hewlett-Packard, employing the electron ionization method at an energy level of 70 electron volts (eV) [16]. Spectra within the wavelength range of 200 to 700 nm for solutions were documented using a UV-Vis PerkinElmer Model spectrophotometer [17]. The antimicrobial research was conducted at the Microanalytical Center of Cairo University [18], while cytotoxicity studies took place at the National Cancer Institute [19], also located at Cairo University. For the characterization of the nano Copper complex, the determination of surface charge and particle size was carried out using a NanoSight NS500 instrument from Malvern Panalytical [20]. The BET surface area and pore volume were established employing a surface area and pore volume analyzer (Quanta Chrome, Nova Touch 4L, USA) utilizing multi-point and DH pore volume methods [21]. Prior to the analysis, the metal complex nanoparticles underwent degassing at 65°C for 1.25 hours to ensure precise measurements. AFM investigations were conducted employing an Oxford-manufactured AFM instrument, specifically the Jupiter XR AFM model, to analyze the morphology of Copper complex nanoparticles [22, 23]. In preparation for TEM analysis, the samples underwent a 10-minute sonication process using an ultrasonic probe sonicator (UP400S, Hielscher, Oderstraße, Teltow, Germany) at a frequency of 55 kHz, an amplitude of 55%, and a cycle of 0.55. Thin film synthesis was accomplished using a Spain coater instrument (Laurell-650Sz, France) under vacuum conditions, with a rotational speed of 750 rpm and a rate of 50µm per 120 seconds. The AFM images and roughness profiles were obtained at a dimension of 47 nm x 47 nm, employing a gold tap, contact mode, and a scanning speed of 0.31 In/S. This analytical approach allowed for a detailed examination of the surface characteristics and morphology of the nickel complex nanoparticles, providing valuable insights into their structural features. Thin films were fabricated using a Spain coater apparatus (Laurell650Sz, France) within a vacuum environment. The process involved maintaining a rotational speed of 750 revolutions per minute (rpm) and achieving a deposition rate of 50 µm every 120 seconds. To evaluate surface wettability, the Biolin Scientific contact angle analyzer (model T200) was employed, operating in a sessile drop configuration [24, 25]. The assessments were performed with a 10-second temporal interval and a droplet volume of 4 µL consisting of distilled water. In the development of Copper complex nanosensors based on quartz crystal microbalance (QCM), an AT-cut quartz crystal chip with a 5 MHz resonance frequency and a 12 mm diameter, affixed to a gold electrode, was utilized (Q-Sense, Shenzhen, China). Before the stabilization of nanomaterials, the gold sensor underwent a cleaning procedure by immersing it in a solution of aqueous ammonia, H_2O_2, and double-distilled water (5:1:1 v/v/v) at 75°C for 10 minutes. Subsequently, the sensor was rinsed with double-distilled water and ethanol and air-dried at room temperature. The dried chip was then inserted into the Q-Sense instrument. Following this, a stream of double-distilled water was introduced over the electrode to serve as a background electrolyte. Introducing the background electrolyte solution, comprising doubly distilled water, into the Quartz Crystal Microbalance (QCM) module initiates baseline measurements before incorporating nanomaterials onto the sensor. To establish a steady QCM signal, a continuous infusion of doubly distilled water is maintained until the signal stabilizes at a recorded zero value. Subsequently, a 2 mL solution of 2 ppm cadmium complex nanoparticles is prepared by mixing with 10 mL of doubly distilled water. Following this preparation, a portion of the mixture is carefully introduced onto the gold sensor at a controlled flow rate of 0.4 mL/min.

Monitoring Cadmium Ion Levels through QCM

The Quartz Crystal Microbalance (QCM) evaluations were executed utilizing a QCM apparatus from Qsenses, Biolin Scientific, situated in Linthicum Heights, MD, USA [26, 27] (see Fig. 2). Each measurement on the Quartz Crystal Microbalance (QCM) involved the introduction of 1 ppm solutions containing cadmium onto the surface of QCM-based nanosensors specifically designed for the detection of cadmium complexes. These measurements were systematically performed under varying concentrations (1, 2, 3 ppm), diverse temperatures (25°C, 35°C, and 45°C), and different pH levels (3.5, 7, and 11). The administration of the cadmium solution was iteratively carried out until the signal stabilized, indicating the achievement of equilibrium in the binding interaction between the Copper Nanosensors and cadmium ions. To purge non-adsorbed particles from the Quartz Crystal Microbalance (QCM) sensor interfaces, a solution of double-distilled water was introduced into the system following a predefined time interval [27, 28]. This method was employed to effectively eliminate any lingering cadmium particles, thereby optimizing the Nano sensors for subsequent measurement procedures.

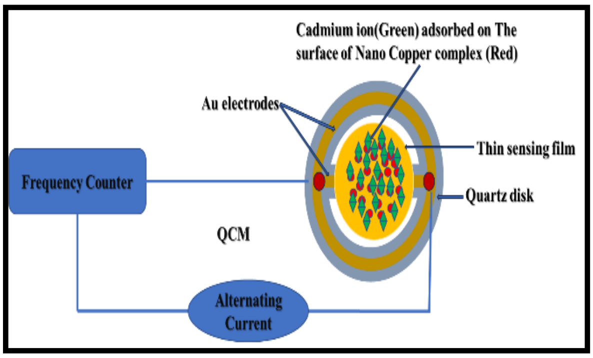


Figure 2. Senses QCM System: Configuring Experiments for Cadmium Detection via QCM Evaluation.

3. Results and Discussion

3.1. Characterization of Schiff base copper complex nanoparticles

3.1.1. Chemical composition and biological properties of Nano Schiff base copper complex

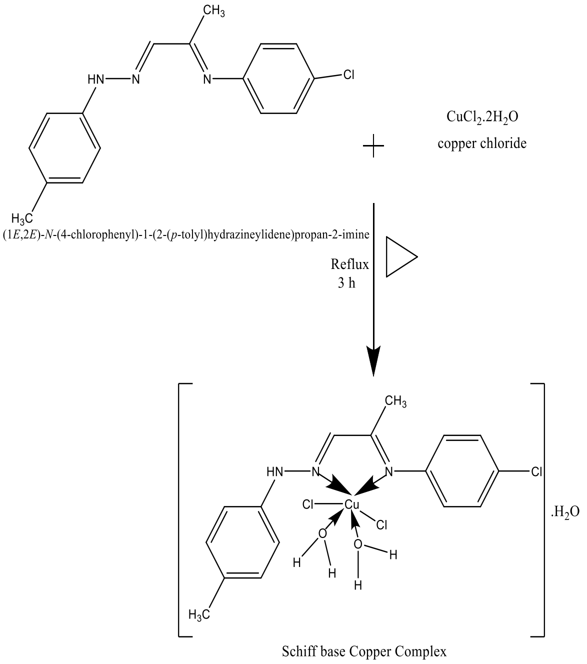
The experimental investigation has substantiated the compound's stability under ambient air conditions, as well as its solubility in diverse polar organic solvents, including ethanol, methanol, dimethylformamide, and dimethyl sulfoxide. Notably, it remains insoluble in aqueous solutions, a characteristic that has been documented in recent publications by researchers [9]. The newly synthesized Schiff base copper complex exhibited favorable characteristics with a yield of 82%, a melting point of 216°C, and presented as a dark green solid. Elemental analysis results were in agreement with the calculated values for **$[Cu(L)Cl_2(H_2O)_2] \cdot H_2O$** with molecular formula **($C_{16}H_{22}Cl_3CuN_3O_3$)**, confirming a 1:1 metal-to-ligand ratio and validating the composition of the complex. Conductivity assessments in dimethyl sulfoxide (DMSO) at a concentration of 10^{-3} M and a temperature of 25 °C indicated a molar conductivity value of 42 Ω^{-1} mol^{-1} cm^{-2}, indicating the non-electrolytic nature of the copper complex [29]. the EI-MS technique was used in this work to corroborate the mass of the copper complex by examining the intense molecular ion peaks in the spectra shown at m/z = 475 $[M+1]^+$. To elucidate the coordination mechanism between the ligand and the copper center, infrared spectra comparisons were conducted. The coordination through the nitrogen atoms of the two azomethine groups was identified, as evidenced by the distinct shift of the strong band at 1608 cm^{-1} corresponding to (C=N) azomethine in the parent ligand to 1617 cm^{-1} in the copper complex [30]. Non-ligand bands corresponding to $\upsilon(M\text{-}N)$ and $\upsilon(M\text{-}O)_{H_2O}$ vibrations were observed at 423 cm-1 and 508 cm-1, respectively [29, 30]. Furthermore, thermal decomposition analysis of the **$[Cu(L)Cl_2(H_2O)_2] \cdot H_2O$** complex revealed a three-step process. The first step, between 35–95°C, involved the loss of water molecules, accounting for a mass loss of 3.572%. The subsequent step, between 95-305°C, included the loss of **$C_7H_{12}ClNO$** with an estimated mass loss of 33.605%, and the final step, between 305–800°C, related to the loss of **$C_9H_8Cl_2N_2$** with an estimated mass loss of 44.78%. After complete decomposition, copper oxide (CuO) remained as residues. In the ultraviolet region, the copper complex exhibited distinctive bands at 245 (π–π*), 285 (π–π*) conjugated, 318(n- π*), and 358 (Charge transfer) [10]. Scheme (1) visually illustrates the structure of the copper Schiff base ligand and its formation reaction. Recent investigations have further explored the antibacterial and antifungal properties of the cobalt complex nanoparticles using the disc diffusion method. The study evaluated various bacterial organisms, including Gram-positive bacteria (Streptococcus mutans, and Staphylococcus aureus), Gram-negative bacteria (Escherichia coli, and Salmonella enterica), and fungal strains (Candida albicans and Aspergillus flavus). The data suggests that the Schiff base copper complex exhibits significant bioactivity against the tested microorganisms, with varying degrees of effectiveness compared to the standard antibiotics and antifungal agents used as references. The complex appears to be particularly effective against the tested fungal strains, Candida albicans and Aspergillus Niger, outperforming the standard antifungal nystatin. [31] Table 1.

Table 1. Antimicrobial Activity of Schiff Base Copper Complex Against Various Microorganisms.

Sample Microorganism	**Schiff base Copper Complex**	**Standard antibiotic**
Gram negative bacteria		Gentamicin
Escherichia coli (ATCC:10536)	19.3±0.6	27.0±1.0
Salmonella enterica (ATCC: 14028)	9.0±1.0	18.3±0.6
Gram positive bacteria		Ampicillin
Staphylococcus aureus (ATCC:13565)	10.0±1.0	22.0±1.0
Streptococcus mutans (ATCC:25175)	22.3±0.6	20.3±0.6
Fungi		Nystatin
Candida albicans (ATCC:10231)	26.7±0.6	21.0±1.0
Asperagillus Nigar (ATCC:16404)	28.3±0.6	19.3±0.6

3.1.2. XRD.

Recent advancements in powder X-ray diffraction (XRD) methodologies have substantially enhanced the analytical capabilities of mineralogists and solid-state chemists in investigating the physicochemical composition of unidentified materials. XRD remains an extensively utilized technique for elucidating the dimensions and geometric characteristics of the unit cell in diverse compounds, providing essential qualitative, quantitative, and multifaceted analytical perspectives [32].



Scheme (1) visually illustrates the structure of the copper Schiff base ligand and its formation reaction.

The X-ray diffraction (XRD) pattern of the nano copper Schiff base sample revealed several prominent diffraction peaks at 2θ angles of 17.749°, 28.313°, 35.561°, 16.041°, and 25.570°, corresponding to d-spacing values of 4.99325 Å, 3.14963 Å, 2.52249 Å, 5.52063 Å, and 3.48090 Å, respectively. The diffraction peaks at 17.749°, 28.313°, and 35.561° could tentatively be assigned to the (111), (220), and (311) crystallographic planes, respectively, indicating the presence of a face-centered cubic (FCC) crystal structure. The peak at 16.041° with a d-spacing of 5.52063 Å may correspond to the (100) plane of a simple cubic structure or a low-index plane of a different crystal system. However, the diffraction peak at 25.570° with a d-spacing of 3.48090 Å did not match any common low-index planes for FCC or simple cubic structures, suggesting a higher-index plane or a plane corresponding to a different crystal structure [32]. (refer to Fig. 3).

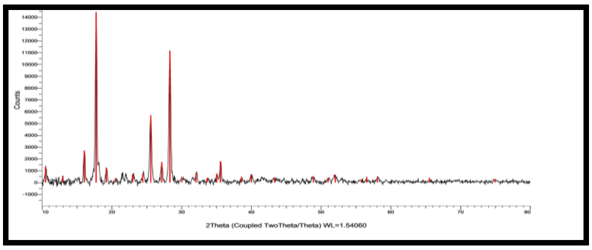


Figure 3: Analysis of Material Composition in the Newly Synthesized Nano Copper Complex Using Powder X-ray Diffraction Methods.

Textural characters SEM of copper complex Nanoparticles

In recent examinations, scanning electron microscopy (SEM) has been employed to investigate the dispersion properties of nanoparticles derived from copper complexes. The SEM images acquired in these investigations revealed a remarkable degree of homogeneity among the fabricated particles, portraying individual entities with a spherical spongy morphology and an absence of apparent aggregation or agglomeration. Furthermore, the determined diameters of these nanoparticles were observed to be below 100 nm, as depicted in Figure 4 [33, 34].

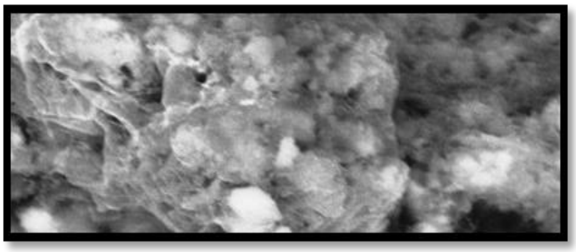


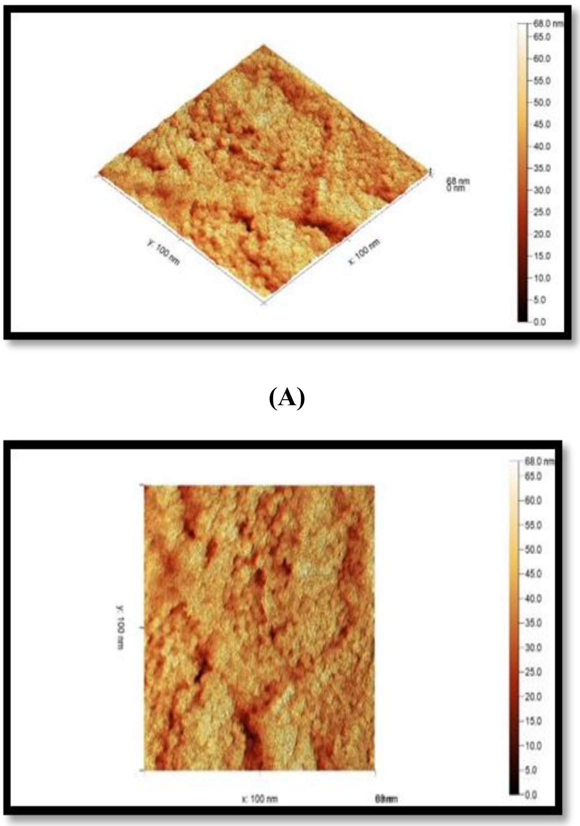
Figure 4. Scanning Electron Microscopy Analysis of Nanoparticles Formed by Copper Complex

Textural characters (AFM) of copper complex Nanoparticles.

The surface attributes of the recently produced Nano copper complex were thoroughly examined using an atomic force microscope (AFM) [35]. AFM images distinctly demonstrated a porous fibrous morphology, as depicted in Figure 5, signifying the conspicuous absence of discernible indications of aggregation or agglomeration. Examination of the AFM imagery facilitated the quantification of particle dimensions, revealing a determined size of 68 nm.

DLS and Zeta Potential

Recent advancements in the characterization of nanoparticles have utilized dynamic light scattering (DLS) to evaluate the particle size of nano cobalt complexes. The analysis revealed an average particle size of 32.6 nm for the nano copper complex as depicted in Fig 6. Subsequent investigations unveiled an unimodal size distribution with low polydispersity indices in the suspension, indicating a uniform particle size distribution. Moreover, the system exhibited remarkable colloidal stability. Insights into the stability of the nano copper complex were elucidated through the examination of particle size distribution and Zeta potential results. The Zeta potential measurement, indicative of a well-dispersed nanoparticle system with a value of -30 mV, underscores the physicochemical stability of the system, particularly under storage conditions. Significantly, findings by Katherina, Javiera, Carlos, Marlene, and Estrella (2016) emphasized that a higher absolute value of Zeta potential corresponds to a higher stable system. Zeta potential serves as a pivotal parameter indicative of the physicochemical stability of nanoparticles, especially during storage conditions (Hamdi, Nasri, Li, & Nasri, 2020). In the case of the nano copper complex, the negative Zeta potential value of -30 mV confirms its heightened stability as illustrated in Fig 7.



(A)

(B)

Figure 5. (A) displays the 3D Atomic Force Microscopy (AFM) representation on the left, whereas (B) illustrates the 3D Two-Dimensional Atomic Force Microscopy (2DAFM) depiction on the right, featuring nanoparticles of the copper complex.

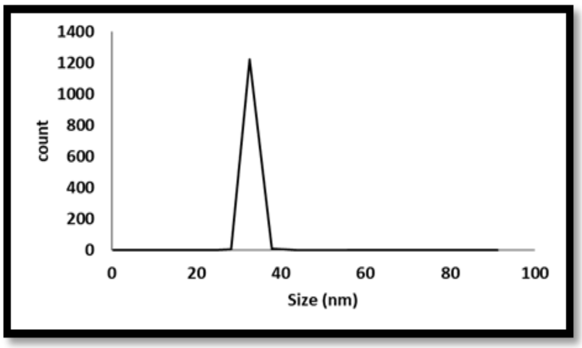


Figure 6. Particle Size Distribution Analysis of Nano Schiff base Copper Complex by Dynamic Light Scattering (DLS).

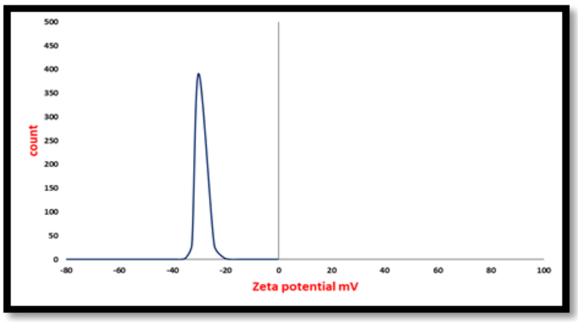


Figure 7. Zeta Potential Analysis Confirms Enhanced Stability of Nano Copper Complex (-30 mV).

BET surface area and pore size

The BET methodology, named in tribute to its developers Brunauer, Emmett, and Teller, serves as an invaluable strategy for elucidating the features of materials at the nanoscale. This approach relies on the phenomenon of physical adsorption of gases onto solid surfaces, providing a rapid, effective, and straightforward means of assessing the surface area of nanostructures [36,37]. In the analysis of the nano copper complex specimen, the application of BET adsorption isotherms played a crucial role in scrutinizing its surface area characteristics. De Boer's classification proves invaluable in stratifying isotherms depicting hysteresis loops, allowing a meticulous assessment of porous configurations. Specifically, the nitrogen adsorption-desorption isotherms exhibited a consistent manifestation of type IV for all nanoparticle samples associated with copper complexes. This observation substantiates the presence of hysteresis loops, confirming the macroporous attributes inherent in these particles. The multipoint BET surface area analysis determined a noteworthy value of 54.7254 m^2/g, accompanied by a corresponding average pore Size of 6.88273 nm and an average particle radius of 2.4918e+001 nm. The substantial surface area, elucidated through multipoint BET analysis (refer to Fig 8), significantly enhances the capacity of metal complex nanoparticles to adsorb cadmium ions within aqueous environments. The macroporous structural characteristics stem from the spherical morphology of these nanoparticles, a feature that markedly amplifies their surface's affinity for cadmium ion adsorption. Crucially, this distinctive macroporous architecture plays a pivotal role in augmenting the efficacy of cadmium ion adsorption by the metal complex nanoparticles.

Contact angle, Hydrophobicity, and toxicity of Nano Schiff base copper complex.

The hydrophobic nature exhibited by the nano copper complex particles is evident from the considerable water contact angle, measuring 113.67° (refer to Figure 9) [38, 39].

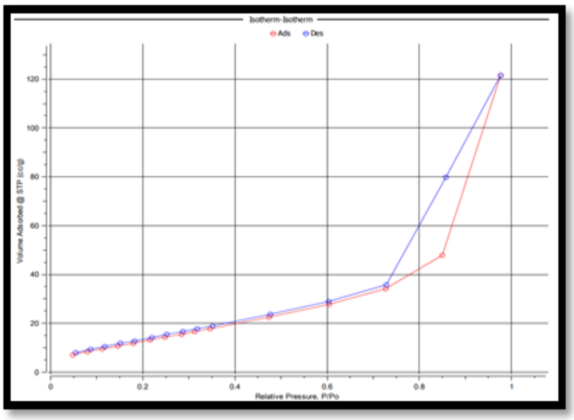


Figure 8. Nano Copper Complex Particle Surface Properties and Adsorption Capacities via BET Analysis.

The experimental protocol involved maintaining a consistent water droplet volume of 0.5 µL, with the contact angle measurement taken precisely 3 seconds after the droplet was dispensed. This procedure was repeated five times under constant room temperature and humidity conditions [38, 39]. This inherent hydrophobic characteristic significantly enhances the appropriateness of these nanoparticles for effective sensing applications in aqueous environments. In the pursuit of developing environmentally friendly nanoparticle-based sensors, it becomes imperative to ensure the non-toxicity of the material. A comprehensive assessment of the cytotoxicity of the Nano Schiff base copper complex yielded a reassuring IC_{50} value of 501.70 µg/ml [40] Fig 10. The notably elevated IC_{50} value instills confidence in the potential utilization of the Nano Schiff base copper complex as a sensor in applications pertaining to water, underscoring its safety and environmental compatibility.

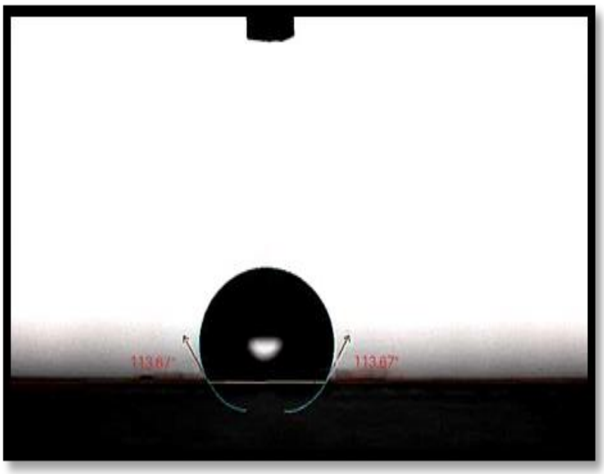


Figure 9. Determining the contact angle between Nano Schiff base copper-complex and water.

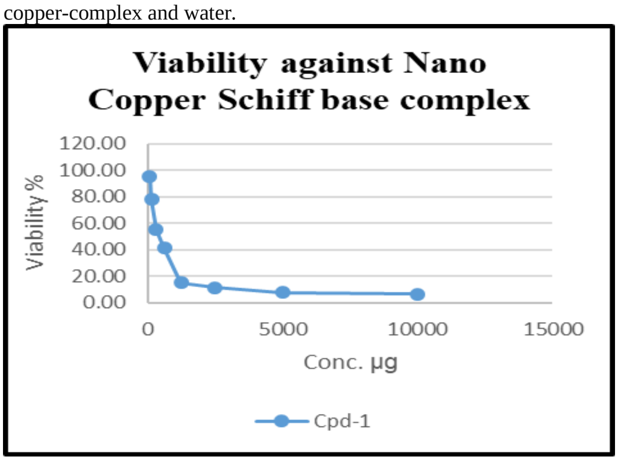


Figure 10. Impact of Nano Copper Complex Cytotoxicity on normal Cell Line Viability.

Monitoring CADMIUM IONS Levels with Nano Sensors Based on Quartz Crystal Microbalance (QCM).

A conventional protocol employing a Quartz Crystal Microbalance (QCM)-based Nano cadmium complex sensor (Fig 11) can be outlined into four discrete stages, each providing fundamental perspectives on the sensor's effectiveness in discerning cadmium ions:

A. Initiation of Baseline Stability: During the initial phase, the sensor's frequency response undergoes comprehensive documentation, serving as a stable reference measurement. This foundational step establishes a benchmark for subsequent phases.

B. Rapid Frequency Decrement upon Binding of Cadmium Ions: A sudden and significant reduction in frequency is observed when cadmium ions swiftly bind to the sensor's surface. This swift alteration is attributed to the occupation of numerous available binding sites on the sensor's surface by cadmium ions.

C. Ongoing Adsorption of Cadmium Ions: Progressing through the experiment, there is continuous adsorption of cadmium ion molecules onto the Nano Schiff base copper complex sensor's surface. This phase highlights the sensor's capacity to capture additional cadmium ions continually.

D. Achievement of Equilibrium State in Adsorption: Ultimately, the adsorption process reaches an equilibrium state between the Nano Schiff base copper complex and cadmium ion molecules. At this juncture, the sensor's frequency shift stabilizes, indicating the attainment of the maximum capacity for cadmium ion adsorption. The accompanying visual representation illustrates the sensor's performance throughout various phases, emphasizing its efficient capture of cadmium ions. The frequency stabilization marks the establishment of equilibrium in the adsorption of cadmium ions on the surface of the QCM-based cadmium complex Nano sensor. In the fourth stage, no discernible alterations in the sensor's frequency are evident, suggesting minimal mass loss and minor structural adjustments to the Nano sensor’s surface.

For real-time Frequency Monitoring of QCM in Nano Copper Complex Interaction with Cadmium Ions: Quantitative Determination of Concentration Using Calibration Curve for:

- Monitor the real-time frequency changes on the QCM in response to the interaction between the Nano cadmium complex and cadmium ions.

- Compare the observed frequency shift with the calibration curve to quantitatively determine the concentration of cadmium ions in the sample. This reasserts the sensor's efficacy in detecting cadmium ions.

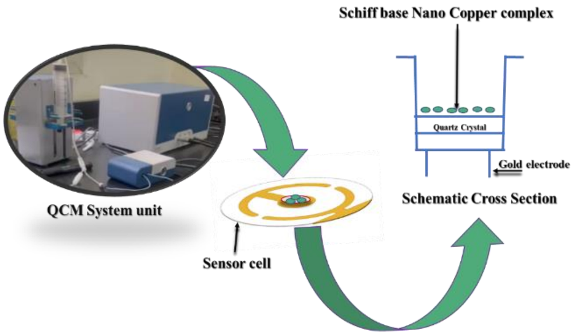


Figure 11. Illustrative image of Schiff base Nano copper complex sensor based on QCM

Suggested Detection Mechanism for Nano Schiff Base Copper Complex Using QCM-Based Sensing

Due to the comparatively lower electronegativity exhibited by CADMIUM IONS in relation to the Nano Schiff base copper sensor, various interaction mechanisms come into play. Initially, dipole-dipole interactions may manifest, potentially accompanied by π–π interactions [41]. Furthermore, the Nano Schiff base copper complex features polar side chains that act as electron-donating groups, resulting in an increased negative charge density on the sensor's surface. Consequently, the QCM-based Nano Schiff base copper sensor exhibits an elevated propensity for engaging with CADMIUM IONS, predominantly through electrostatic interactions, in conjunction with the π–π interactions [41].

Effect of concentration

Figure 12 portrays the response of the Nano Copper (II) Schiff base complex to Cadmium ions using a QCM-based sensor assessment methodology. The graphical representation illustrates alterations in resonance frequency (Δf) for the Nano Copper (II) Schiff base complex at different concentrations, highlighting its proficiency in detecting varied concentrations of investigated cadmium ions (1, 2, and 3 PPM). Notably, all concentrations exhibit a consistent trend of resonance frequency changes (Δf), with frequency modulation occurring within a brief temporal window of approximately 2 minutes.

Effect of pH

The initial pH level of a sorbent plays a pivotal role in the adsorption of metal ions, exerting substantial influence on two critical facets: the chemical speciation of metal ions in the solution and the ionization of functional groups present on the surface of the adsorbent. These significant factors were underscored by Petrovi et al. in their 2016 research. In order to investigate the impact of pH on the adsorption of cadmium ions [42-44], a series of meticulously conducted batch experiments were undertaken at varying pH values, specifically at 3.5, 7, and 11. In accordance with the graphical representation in Figure 13, the peak of adsorption on the adsorbents manifestly occurred within the pH range of 3.45 to 6. Notably, a significant decline in adsorption was observed when pH values deviated below this specified range, whereas at elevated pH values, the reduction in adsorption exhibited a comparatively moderate trend. Concerning the adsorption of Cadmium ions, as depicted in Figure 3a, the pinnacle of adsorption was discernible at pH values approximately around 6.7, coupled with a conspicuous reduction in adsorption at lower pH values, particularly those falling below 3.45. The diminished sorption observed at lower pH levels, as elucidated by Low et al. in 1993, is attributed to competitive interactions between hydrogen ions and metal ions. In an acidic environment characterized by a lower pH, there is an elevated concentration of H^+

ions, which exhibit a heightened affinity for adsorption points, surpassing that of heavy metal ions. Consequently, H^+ ions engage in competitive interactions, seizing a greater number of adsorption sites. These ions vie for the available binding sites on the biosorbent's surface. Conversely, within the pH range of 2.0 to 4.0, a significant event occurs in the deprotonation of carboxylic groups on the sorbent's surface. This deprotonation amplifies the adsorption of metals, a phenomenon substantiated by the investigations of Chang et al. in 1997 and Chen et al in 2010. In the pH range spanning from 4 to 6, a subtle augmentation in the extraction of metals becomes apparent. This can be attributed to the observation that the adsorption sites on the sorbent's surface exhibit reduced sensitivity to pH-induced changes within this interval. Conversely, an elevation in pH levels results in noticeable cadmium leaching

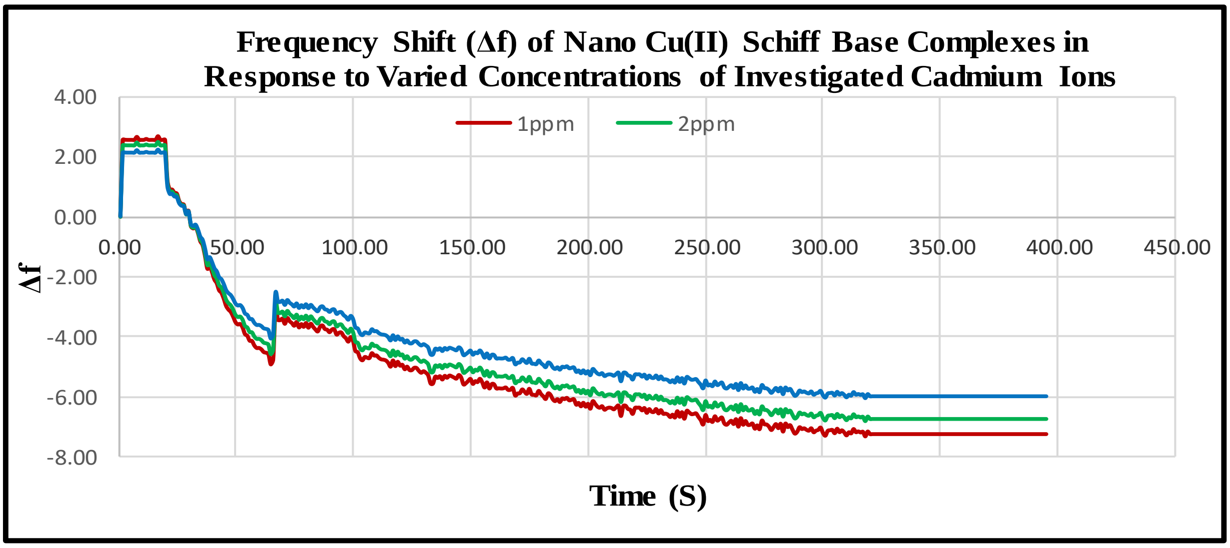


Figure 12. Quartz Crystal Microbalance (QCM) Sensor Output of the Nano Copper (II) Schiff base complex for Different Concentrations of Cadmium Ions (1, 2, and 3 PPM).

This, in turn, diminishes the adsorption rate, thereby reducing the sorbent's capacity to effectively eliminate heavy metals, as depicted in Figure 8. This phenomenon can be further expounded by considering the heightened presence of sodium ions (Na^+) in the solution due to pH adjustments. These sodium ions compete with the remaining cadmium ions for the accessible exchangeable sites on the sorbent's surface, contributing to the observed effect.

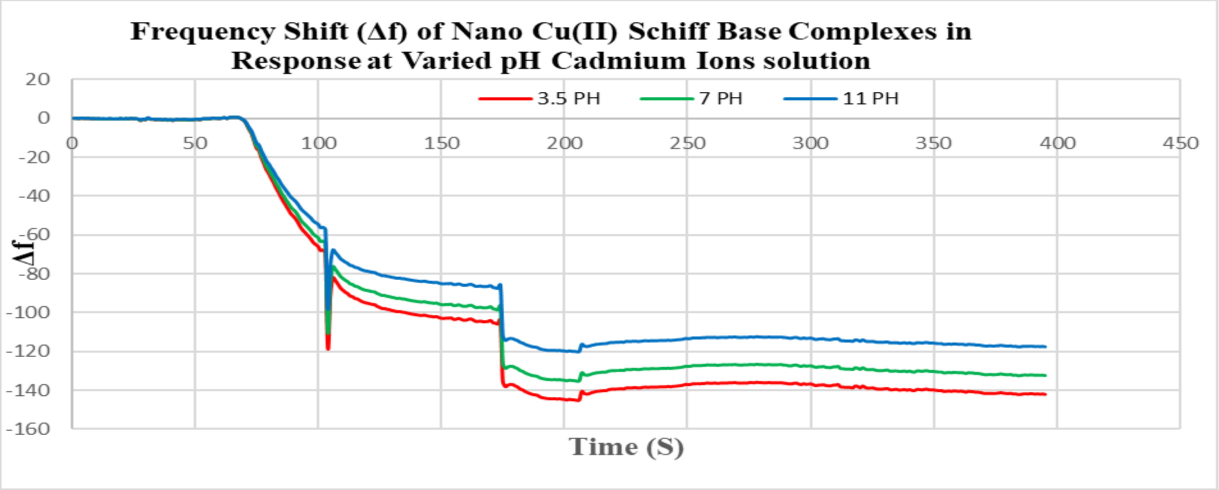


Figure 13. Quartz Crystal Microbalance (QCM) Sensor Output of the Nano Copper (II) Schiff base complex for Different pH of Cadmium Ions (3.5, 7, and 11 PPM).

4. Conclusion

This study introduces an innovative nanosensor based on a newly synthesized Nano Schiff base copper complex for the reliable detection of cadmium ions in water reservoirs. The characterization of the Nano copper sensor through Dynamic Light Scattering (DLS) and Zeta potential analysis reveals a particle size distribution of 32.6 nm and zeta potentials of -30 mV. Scanning Electron Microscopy (SEM) and Atomic Force Microscope (AFM) examinations further illustrate a consistently spongy fibrous morphology of the nanoparticles at the Nano scale, with a particle size dimension of 68 nm. The synthesized nanomaterials are then employed in the fabrication of advanced nanosensors using the Quartz Crystal Microbalance (QCM) method. These engineered nanosensors are subsequently employed to detect low concentrations of cadmium ions, achieving sensitivity down to 1 ppm. The assessments are conducted under various conditions, including different concentrations (25°C, 35°C, and 45°C) and pH levels (3.5, 7, 11). In summary, the Nano Schiff base copper complex nanoparticles, synthesized using the QCM approach, exhibit remarkable efficacy as real-time, rapid (with a response time of just 2 minutes), and highly sensitive nanosensors for the continuous-flow detection of cadmium ions in water sources and diverse environmental samples.

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