



CHROMIUM COMPLEX NANOPARTICLES SENSOR FOR ARSENIC DETECTION USING QCM TECHNIQUE

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Abstract

In recent times, there has been a significant rise in global arsenic intake, stemming from both drinking water and food sources. Arsenic contamination in groundwater can originate from natural geological processes as well as industrial effluents, agricultural practices such as insecticide use, municipal sewage, and household waste. One eco-friendly and dependable method for addressing this issue involves the synthesis of metal complex nanoparticles, which has broad applications in various fields. A noteworthy development is the creation of a novel nano chromium sensor designed specifically for detecting arsenic. This Nano chromium complex underwent comprehensive characterization using a range of analytical tools, including Dynamic Light Scattering (DLS), Zeta potential analysis, Transmission Electron Microscopy (TEM), scanningelectron Microscopy (SEM), Fourier-Transform Infrared Spectroscopy (FT-IR), contact angle measurements, as well as BET surface area and pore size determination. Furthermore, researchers explored the practical application of the Nano chromium complex as a simple, cost-effective, and highly sensitive Quartz Crystal Microbalance (QCM) sensor for the rapid detection of arsenic. Using this nano chromium complex sensor, arsenic can be reliably detected even at extremely low concentrations, as low as 1 ppm, with a remarkable response time of just 1 minute. Additionally, the cytotoxicity of the arsenic complex nanoparticles was thoroughly investigated to ensure their safety. This innovative method has demonstrated its effectiveness and feasibility for the precise determination of arsenic ions in samples from groundwater and industrial effluent wastewater.

Keywords: Arsenic; chromium complex; Nanoparticles QCM sensor; TEM; BET; contact angle

1. Introduction

Arsenic, a toxic trace element found ubiquitously in the environment, poses a serious health risk even in minute quantities. Its toxicity is attributed to its ability to bind to and inhibit enzymes crucial for normal bodily functions [1]. Arsenic is naturally present in water, soils, rocks, and all living organisms, including plants and animals. It accumulates in the body over time, affecting various physiological systems [2–4]. Given its high toxicity, regular monitoring and removal of arsenic from various sources, such as natural waters, are imperative. The World Health Organization (WHO) has recently set a stringent limit of 10 ng/mL for total arsenic in drinking water [5], demanding the use of highly sensitive analytical techniques. Several analytical methods have been employed for trace arsenic determination, including colorimetry [6, 7], atomic absorption spectrometry [7, 8], hydride generation systems combined with atomic absorption spectrometry [9], inductively coupled plasma mass

spectrometry [10, 11], and atomic fluorescence spectrometry. In complement to these instrumental methods, nanoparticles-based sensors have proven to be effective tools for predicting the accumulation, translocation, and eco-toxicological impacts of heavy metal pollution [3]. Among these, the Nanoparticles-based Quartz Crystal Microbalance (QCM) sensor has gained significant attention due to its advantages such as affordability, selectivity, sensitivity, and rapid response time. Consequently, there is a pressing need for a swift, dependable, and highly sensitive sensor for arsenic detection. Our current research endeavors focus on developing a single analytical sensor capable of detecting heavy metals like arsenic.

2. Materials and methods

2.1. Experimental

2.1.1. Preparation of Nano chromium complex.

The synthesis of the Nano chromium complex followed a series of steps. Initially, a hot Ethanolic solution at 70°C containing the Schiff base ligand Fig (1) (1 mmol, 0.442 g) was prepared.

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In a separate hot absolute ethanol solution (20 ml), the metal salt (0.266 g $\text{CrCl}_3 \cdot 6 \text{H}_2\text{O}$) was dissolved. After three hours of continuous stirring under reflux conditions, the resulting complex began to precipitate from the solution. These precipitates were subsequently collected via filtration, subjected to thorough washing, and finally dried under a vacuum using anhydrous calcium chloride. The purification process was completed through recrystallization. Remarkably, during this procedure, the color of the complex transformed from dark green to brown. Additionally, the formed complex underwent ultrasonic probe treatment for 10 minutes [12].

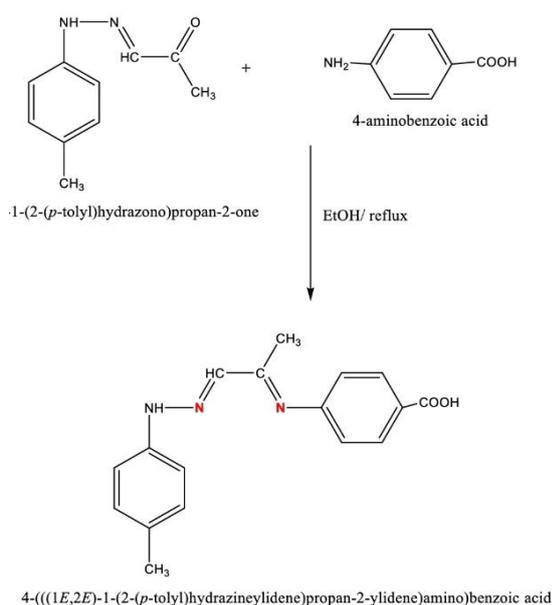


Figure 1: Schiff base ligand (L)

2.1.2. Instrumentation

The research conducted at Cairo University in Egypt involved a variety of scientific instruments and techniques for analyzing and characterizing materials, as well as studying their properties. Here's a rewritten summary:

A CHNS-932 (LECO) Vario Elemental analyzer at Cairo University's Microanalytical Center was employed to perform microanalysis, specifically for carbon, hydrogen, and nitrogen content determination. The melting point of the materials was determined using a triforme XMTD-3000 apparatus. Fourier transform infrared (FT-IR) spectra were acquired using a Perkin-Elmer 1650 spectrometer with KBr disks, covering the range of $4000\text{--}400 \text{ cm}^{-1}$. To measure the molar conductance of solid complex solutions in ethanol at a concentration of 10^{-3} M , a Jenway 4010 conductivity meter was used.

Mass spectra were obtained using an MS-5988 GS-MS instrument from Hewlett-Packard, utilizing the electron ionization method at 70 eV. A UV-Vis PerkinElmer Model spectrophotometer was employed to record the spectra of solutions within the wavelength range of 200 to 700 nm. The antimicrobial research was conducted at Cairo University's Microanalytical Center, while the cytotoxicity studies were carried out at the National Cancer Institute, also at Cairo University. For nano chromium complex characterization, the surface charge and particle size were determined using a NanoSight NS500 instrument from Malvern Analytical. The BET surface area and pore volume were determined using a surface area and pore volume analyzer (Quanta Chrome, Nova Touch 4L, USA) with the multi-point and DH pore volume methods. The metal complex nanoparticles were degassed at 65°C for 1.25 hours before analysis.

Further analysis of the samples was conducted using a JEOL JEM-2100 high-resolution TEM instrument from Peabody, MA, USA. Prior to TEM analysis, the nanoparticles underwent sonication for 15 minutes using an ultrasonic probe sonicator (UP400S, Hielscher, Teltow, Germany) at a frequency of 55 kHz, an amplitude of 55%, and a cycle of 0.55.

Thin film synthesis was performed using a Spain coater instrument (Laurell650Sz, France) at a vacuum condition with a speed of 750 rpm and a drop rate of $50 \mu\text{m}$ per 120 seconds.

To measure wettability, a Biolin Scientific (model T200) contact angle analyzer was used under sessile drop conditions, with a measurement time of 10 seconds and a droplet volume of $4 \mu\text{L}$ of distilled water. Establishing of QCM-Based chromium 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, H_2O_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 chromium 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.

2.1.3. QCM-Monitoring of arsenic ions.

Certainly, here's a rewritten version with reference numbers for each piece of related information: The QCM measurements were conducted utilizing a QCM system (QCM, Qsenses, Biolin Scientific, Linthicum Heights, MD, USA)[13]. Each QCM measurement involved injecting 1 ppm of arsenic solutions onto the surface of either QCM-based chromium complex nanosensors. These measurements were carried out at various temperatures (25°C, 35°C, and 45°C) and different pH levels (4, 7, and 10). The arsenic solution was repeatedly injected until the signal stabilized, indicating that the equilibrium of the binding interaction between the nanosensors and the arsenic ions had been reached. To remove unadsorbed particles from the surfaces of the QCM sensors, double-distilled water was poured into the module after a predetermined amount of time [13].

3. Results and Discussion

3.1. Characterization of chromium complex nanoparticles.

The Nano chromium complex is characterized by its chemical composition and notable biological properties. This complex is air-stable and readily soluble in polar organic solvents such as ethanol (EtOH), methanol (MeOH), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO). However, it exhibits poor solubility in water [14]. Elemental analysis confirms a 1:1 metal-to-ligand ratio for this complex. Its molar conductivity (Λ_m) in DMF (at a concentration of 10–3 M) at 25 °C is $105 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$, indicating its electrolyte nature [15]. The coordination mechanism of the ligand to the chromium center can be elucidated by comparing the infrared spectra of the parent ligand and the chromium complex. Notably, the azomethine group in the ligand exhibits a strong band at 1608 cm^{-1} , which shifts to 1590 cm^{-1} in the complex, indicating coordination through the nitrogen atoms of the azomethine groups. Nonligand bands in the range of 416 cm^{-1} and 544 cm^{-1} correspond to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ coordinated water, respectively [16]. Based on this data, the suggested formula for the chromium complex is $[\text{Cr}(\text{L})\text{Cl}_2 \cdot 2\text{H}_2\text{O}]\text{Cl} \cdot \text{H}_2\text{O}$ [17]. The UV-Vis spectrum of the chromium complex reveals strong characteristic bands at 215 nm, 260 nm, and 357 nm, corresponding to $\pi-\pi^*$ and $n-\pi^*$ intramolecular transitions [18].

In terms of biological activity, the chromium complex's antibacterial and antifungal properties were assessed using the disc diffusion method. The complex displayed high efficacy against both 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*) [19].

3.1.2. Textural characters (TEM and SEM) of chromium complex Nano particles. The Scanning Electron Microscopy (SEM) Fig (2) and Transmission Electron Microscopy (TEM) Fig. (3) Images of the chromium complex provide visual evidence of the excellent dispersity of the synthesized particles. These images reveal that the individual particles adopt a spherical shape and exhibit no apparent signs of aggregation or agglomeration. Furthermore, the particles have diameters that are consistently smaller than 100 nm [20].

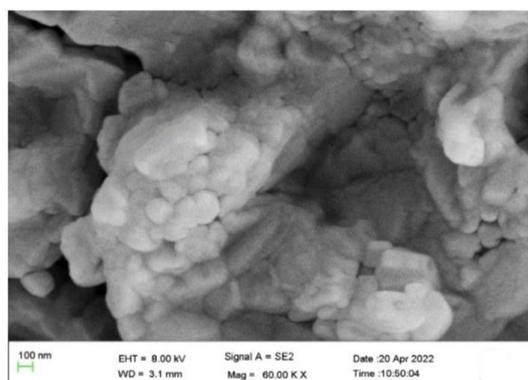


Figure 2: SEM Imaging Reveals Well-Dispersed Spherical Copper Complex Nanoparticles with Sub-100 nm Diameters.

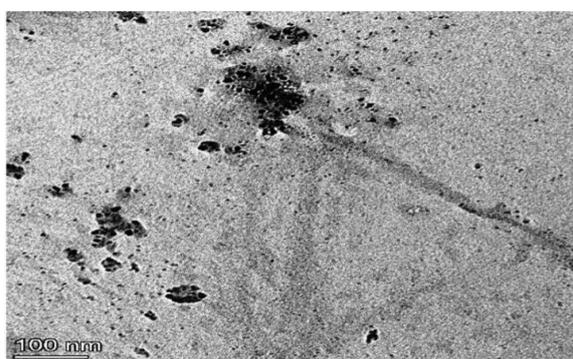


Figure 3: TEM Imaging Reveals Spherical Nanoparticles with Excellent Dispersity in Copper Complex.

3.1.3. DLS and Zeta Potential

The DLS (Dynamic Light Scattering) technique was employed to assess the particle size of a nano chromium complex Fig(4). The analysis revealed that

the nano chromium complex exhibited an average particle size of 56 nm. These findings further demonstrated that the suspension of the nano chromium complex displayed a unimodal size distribution with a low polydispersity index, signifying a remarkably high level of colloidal stability. In Fig(4), both the particle size distribution and Zeta potential results of the nano chromium complex are depicted. Notably, the Zeta potential measured -24 mV, which is indicative of the uniform dispersion of nanoparticles. Zeta potential plays a crucial role in gauging the physicochemical stability of nanoparticles during storage [21]. It is worth noting that the higher the absolute value of Zeta potential, the greater the overall system stability [22]. As the results presented here clearly indicate, the nano chromium complex exhibits an exceptionally high level of stability.

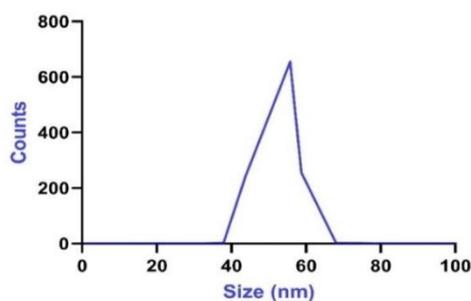


Figure 4: Particle Size Distribution and Zeta Potential Analysis of Nano Chromium Complex.

3.1.3. BET surface area and pore size.

The BET method, named after its creators Brunauer, Emmett, and Teller, is a valuable technique for characterizing materials at the nanoscale. This method relies on the physical adsorption of gases onto solid surfaces, providing an efficient, rapid, and straightforward means of determining the surface area of nanostructures [23]. In the study of the nano chromium complex sample, BET adsorption isotherms were employed to assess its surface area characteristics.

De Boer's classification categorizes hysteresis loop isotherms into four types to determine porous structures. Notably, each sample of chromium complex nanoparticles exhibited type IV nitrogen adsorption-desorption isotherms with hysteresis loops, confirming their macroporous nature. The multipoint BET surface area was found to be 76 m²/g, and the pore volume, determined using the DH (Dubinin-Harkins) method, measured at 24.88 cc/nm. This significant multipoint BET surface area enhances the capacity of metal complex nanoparticles to adsorb arsenic ions in aqueous solutions. The presence of macroporosity can be

attributed to the spherical morphology of the metal complex nanoparticles. Importantly, this macroporous structure enhances the adsorption of arsenic ions on the surface of the metal complex nanoparticles.

3.1.4. Contact angle, Hydrophobicity and toxicity of chromium nano complex.

The nano chromium complex particles demonstrated hydrophobic characteristics, as evidenced by a substantial water contact angle of 126° Fig (6) [24]. This inherent hydrophobicity enhances the applicability of these nanoparticles as efficient sensors in aqueous environments.

In the pursuit of developing environmentally friendly nanoparticle-based sensors, it is imperative to ensure the material's non-toxicity. A comprehensive cytotoxicity assessment of the nano chromium complex yielded a reassuring IC₅₀ value of 310 µg/ml [25]. This notably high IC₅₀ value encourages the utilization of the nano chromium complex as a sensor for water-related application.

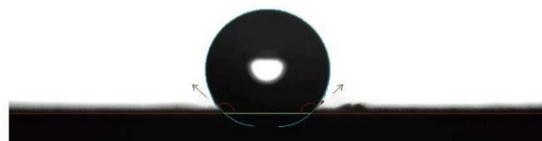


Figure 5: Water Contact Angle Measurement of Nano Chromium Complex Particles.

3.1.5. ARSENIC IONS Monitoring Using QCM-Based Nano chromium sensors.

A typical experiment utilizing a Quartz Crystal Microbalance (QCM)-based nano chromium complex sensor can be divided into four distinct stages, each revealing crucial information about the sensor's performance in detecting arsenic ions[26]:

- Baseline Stability:** In the initial stage, the sensor's frequency response is recorded, providing a stable baseline measurement. This step serves as a reference point for the subsequent stages.
- Rapid Frequency Drop upon Arsenic Ion Binding:** A sudden and significant decrease in frequency is observed as arsenic ions swiftly bind to the sensor's surface. This rapid change is attributed to the occupation of numerous vacant sites on the sensor's surface by arsenic ions.
- Continued Adsorption of Arsenic Ions:** As the experiment progresses, further adsorption of arsenic ion molecules takes place on the nano chromium complex sensor's surface. This stage demonstrates the sensor's ability to capture additional arsenic ions.
- Equilibrium State of Adsorption:** Eventually, an equilibrium state is

achieved in the adsorption process between the nano chromium complex and arsenic ion molecules. The sensor's frequency shift stabilizes at this point, indicating that the maximum capacity for arsenic ion adsorption has been reached. The figure accompanying this description visually illustrates the sensor's performance throughout these stages, showcasing its capacity to effectively bind arsenic ions. Once the frequency stabilizes again, it signifies the attainment of an equilibrium state in the adsorption of arsenic ions on the QCM-based chromium complex nanosensor's surface [26]. At this fourth stage, no noticeable changes in the sensor's frequency are observed. This implies that minimal mass loss has occurred, and any structural modifications to the nanosensor's surface are minor. Consequently, this reaffirms the sensor's effectiveness in the detection of arsenic ions [26].

3.1.6. Proposed Sensing Mechanism of the QCM-Based nano chromium complex

Due to the lower electronegativity of ARSENIC IONS in comparison to the nano chromium sensor, various interaction mechanisms come into play. Firstly, dipole-dipole interactions may arise as a consequence, likely complemented by π - π interactions [27]. Additionally, the presence of polar side chains in the nano chromium complex, serving as functional groups with electron-donating properties, contributes to an increased density of negative charge on the sensor's surface. Consequently, the QCM-based nano chromium sensor exhibits a heightened propensity for interaction with ARSENIC IONS, primarily through electrostatic interactions, alongside the π - π interactions [27].

3.1.7. Effect of temperature

Chemical reactions are known to be significantly influenced by temperature, and the rate of a reaction can be improved or inhibited depending on the surroundings of the reactants and/or products [28]. When the temperature is increased, the reactant particles move faster, resulting in a higher frequency of collisions and a higher reaction rate [28].

In the context of adsorption, the diffusion of the adsorbate molecule is accelerated through the adsorbent's exterior boundary layer and within its pores due to temperature changes [29]. The increased kinetic energy of the molecules at higher temperatures causes them to move more quickly [29]. Additionally, changing the temperature can enhance the adsorbent's capacity to reach equilibrium for a given adsorbate [29].

The influence of temperature on the monitoring of ARSENIC IONS was investigated using a nano chromium complex sensor at different temperatures

(25°C, 35°C, and 45°C) [26]. The results of this study revealed that the detection sensitivity of ARSENIC IONS in aqueous solutions is affected by the temperature of the medium Fig. (7) [26].

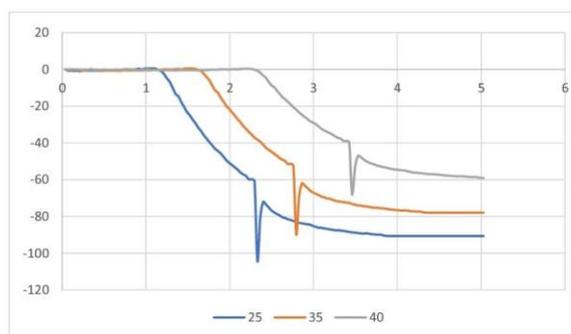


Figure 7: Influence of Temperature on ARSENIC IONS Detection Sensitivity.

Investigating the influence of temperature on ARSENIC IONS monitoring using a nano chromium complex sensor at different temperature levels (25°C, 35°C, and 45°C) revealed intriguing findings [30]. Contrary to the behavior observed in typical QCM-based nano chromium sensors, where frequency shifts increase progressively, our study demonstrated that as the temperature increased from 25°C to 45°C, an increase in frequency shifts occurred.

This unexpected behavior can be attributed to the electrostatic attraction mechanism governing the binding between the highly negatively charged surface of the QCM-based nano chromium sensor and the positively charged ARSENIC IONS molecules. With rising temperatures, there was a greater diffusion of ARSENIC IONS molecules within the solution, which reduced their attachment to the sensor's surface. Additionally, the elevated temperature may have induced bond splitting within the reactive groups on the sensor's surface, leading to a reduction in the number of active adsorption sites. This reduction, in turn, resulted in a decrease in the amplitude of ARSENIC IONS adsorption. Furthermore, our observations indicated that higher temperatures had a negative impact on the adsorption of metal ions in general, as metal ion adsorption decreased with increasing temperature. Notably, the adsorption of ARSENIC IONS on the QCM-based nano chromium sensor's surface caused significant changes in frequency due to the mass of ARSENIC IONS adsorbed onto the sensor's surfaces.

3.1.7. Effect of pH

The initial pH level of a sorbent plays a pivotal role in metal adsorption due to its profound influence on two critical factors: the chemical speciation of metal ions in the solution and the

ionization of functional groups on the adsorbent's surface, as emphasized by Petrovi et al. in their study from 2016. To delve into the impact of pH on the adsorption of arsenic ions, a series of batch experiments were meticulously conducted at varying pH values, specifically 4, 7, and 10.

As illustrated in Figure 3a, the apex of adsorption on the adsorbents was conspicuously observed within the pH range of 4 to 6. Notably, as pH values were reduced below this range, a substantial decline in adsorption occurred, while at higher pH values, the decrease in adsorption was comparatively modest. In the case of zinc ions, Figure 3a graphically depicts that the zenith of adsorption was evident at pH values hovering around 7, with a marked decrease in adsorption observed at lower pH values, particularly below 4.

The rationale behind the limited sorption at lower pH values, as elucidated by Low et al. in 1993, stems from hydrogen ions engaging in competitive interactions with metal ions, vying for the available binding sites on the biosorbent's surface. Conversely, within the pH spectrum ranging from 2.0 to 4.0, a notable occurrence transpired: the deprotonation of carboxylic groups on the sorbent's surface, thereby facilitating an enhanced adsorption of metals, as also corroborated by the findings of Chang et al. in 1997 and Chen et al. in 2010.

Within the pH interval of 4 to 6, a subtle upswing in metal removal was discernible. This phenomenon might be attributed to the fact that the adsorption sites on the sorbent's surface exhibited a reduced susceptibility to pH-induced alterations.

Conversely, when the pH level was elevated, leaching of arsenic became apparent. This resulted in a decreased rate of adsorption, consequently diminishing the removal capacity of heavy metals, as visually depicted in Fig (8). This effect could also be expounded upon by considering the augmented presence of sodium ions (Na⁺) in the solution, attributed to pH adjustments, which competed with the remaining arsenic ions for the available exchangeable sites on the sorbent's surface.

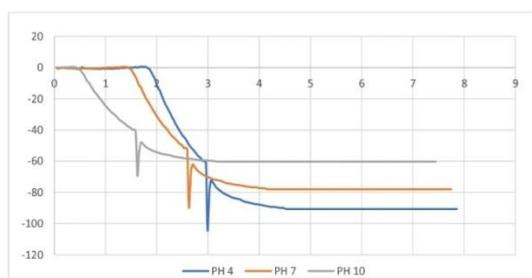


Figure 8: Imaging reveals the impact of pH on Arsenic Leaching and Metal Removal.

4. Conclusion

In this study, a novel nano chromium sensor was developed for the reliable detection of ARSENIC IONS in water sources. Analysis of Dynamic Light Scattering (DLS) and Zeta potential values indicated that the nano chromium sensor exhibited a particle size distribution of 56 nm and had zeta potentials of -24mV. Moreover, observations from Transmission Electron Microscopy (TEM) and scanning electron microscopy (SEM) revealed a consistent spherical shape of the nanoparticles.

Subsequently, these synthesized nanomaterials were employed to create innovative nanosensors using the Quartz Crystal Microbalance (QCM) method. These designed nanosensors were then utilized to monitor low concentrations of ARSENIC IONS, as low as 1 ppm, at various temperatures (25°C, 35°C, and 45°C) and pH levels (4, 7, 10).

In conclusion, the QCM-based chromium complex nanoparticles proved to be highly efficient as real-time, rapid (with a response time of just 1 minute), and sensitive nanosensors for detecting ARSENIC IONS in continuous-flow water sources and various environmental samples.

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