

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/



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



M.S.A. Mansour*, Abeer Taha Ibrahium, Walaa H. Mahmoud, Ahmed A. El-Sherif

Chemistry Department, Faculty of Science, Cairo University, Giza, 12613 Egypt

Abstract

Lead is an elemental substance with inherent toxicity that occurs naturally within the Earth's lithosphere. Its extensive utilization has led to widespread environmental pollution, human contact, and notable global public health effects across various regions. Continuous surveillance of "lead" concentrations in the ecosystem is imperative to minimizing potential hazards and human contact. This research delineates the synthesis and analysis of an innovative Schiff base ligand along with its corresponding ternary Co(II) complex, followed by its nanostructure's fabrication, characterization, and utilization. A Cobalt (II) coordination compound featuring a principal ligand denoted (LAMS) and an auxiliary ligand Methionine denoted (LMET) was synthesized and subjected to comprehensive characterization utilizing various analytical techniques, including FT-IR, UV-Vis, mass spectrometry, elemental analysis, and electric conductance measurements. Thermal behavior analysis (TGA) of the Cobalt (II) complex corroborated well with the proposed formula derived from the analytical data. Characterization outcomes revealed the molecular formula of the Cobalt (II) complex to be [(LAMS)(LMET)Co(Cl)].3H2O. The ligand (LAMS) exhibited tridentate chelation behavior by coordinating with the central Cobalt (II) metal ion through its two azomethine nitrogen groups, while (LMET) bound to the cobalt (II) metal ion via deprotonated hydroxyl oxygen and NH2 group, resulting in a distorted octahedral structure. The extensive characterization of the Nano Schiff base cobalt complex involved a variety of analytical techniques, including Dynamic Light Scattering (DLS), Zeta potential analysis, Atomic Force Microscopy (AFM), BET surface area determination, and pore size analysis. Furthermore, the potential application of the Nano Schiff base Cobalt complex as the Quartz Crystal Microbalance (OCM) stands out among sensing apparatuses, boasting a well-established status and acknowledged sensitivity in detecting molecules and biological assemblies. Renowned for its simplicity and cost-effectiveness, the QCM sensor holds promise, primarily focusing on detecting water contamination by Lead ions. The sensor's mechanical stability was also affirmed by investigating the applied ionophore's lipophilicity using contact angle measurements, revealing an average contact angle of 121.59°. Notably, this attribute contributes to the robustness of the sensor. The sensor's responsiveness under differing pH and temperature conditions was carefully monitored, with a swift response time of less than 1 minute.

Keywords: : lead; Nanoparticles; QCM sensor; AFM; BET; Zeta potential; Schiff base

Introduction

In recent years, lead contamination has been evident in atmospheric air, soil compositions, and drinking water samples. Additionally, traces of lead have been detected in various vegetables and food items [1]. Lead is emitted into the atmosphere through processes such as lead extraction in mining operations, industrial activities employing lead-based compounds, the utilization of lead alloys, vehicular emissions containing lead, and the combustion of fossil fuels [2]. Lead is actively scavenged from the atmosphere through rain, where it is subsequently deposited onto soil or introduced into surface water bodies. Additionally, lead is a pesticide in cultivating vegetables and fruits [3]. Lead is a naturally occurring element in the human body, found in various organs such as the brain, liver, kidneys, and bones. It has an affinity for bone and dental tissue, where it is primarily stored. However, typical lead levels in adults are around 10 micrograms per deciliter (μ g/dL) and 1.4 μ g/dL in children [4, 5]. Prolonged exposure to lead significantly influences the normal operation of the nervous system. Lead functions as a calcium analog, facilitating absorption, particularly in individuals experiencing deficient Ca, Zn, and Fe. It exerts notable impacts on the reproductive systems of both genders [6, 7, 8]. Contemporary research has focused on hybrid ligand complexes comprising amino acid moieties and aromatic amine ligands coordinated with metal ions, exploring their respective biological effects [9]. Schiff base derivatives are effective coordinating agents for transition metals and main group elements in bioinorganic and coordination chemistry [10]. The coordination of Schiff bases with metal ions results in diverse

complexes exhibiting various geometries, which find applications in fields such as oncology, microbiology, virology, pharmaceutical design, organometallic anticancer agents, catalysis, analytical chemistry, mineralogy, and corrosion prevention [11, 12]. Currently, measuring metal ion concentrations in water involves using expensive and complex techniques such as chromatography and spectroscopy. These techniques require extensive technical expertise and are time-consuming. As it is important to monitor the presence of toxic metals in water and the environment, it is necessary to develop sensors designed specifically for this purpose. Recently, chemical sensors based on Nano and functional materials have emerged as promising alternatives for detecting heavy metals. These sensors offer several benefits, including heightened selectivity, sensitivity, portability, on-site sensing capabilities, and enhanced device performance [13]. Nanoparticle-based sensors have a significant advantage due to their high sensitivity and selectivity. They can detect specific heavy metals in complex environmental samples, which is crucial for evaluating heavy metal pollution's bioavailability and potential risks [14]. Nanoparticle-based sensors can be designed to specifically target harmful heavy metals such as lead, cadmium, mercury, and arsenic. These metals are known to affect human health and the environment adversely. This specificity enables accurate and reliable monitoring of heavy metal contamination in various environmental matrices, including water, soil, and air [15]. Fielddeployable devices can integrate nanoparticle-based sensors that offer real-time on-site monitoring, facilitating timely interventions and management strategies for heavy metal pollution assessment in different environmental settings [16, 17, 18]. The Quartz Crystal Microbalance (QCM) technology is a highly promising sensor technology that offers several advantages, such as cost-effectiveness, rapid responsiveness, portability, label-free real-time operation, and notable sensitivity. As a result, it is very well-suited for online detection of analytes with high precision. This makes it a considerable candidate for the development of advanced sensor systems in the future [19]. The prompt is about developing a fast sensor method to detect lead concentrations in drinking water, which is crucial for early detection of lead poisoning and continuous monitoring to prevent health risks. Our ongoing research aims to devise a unified analytical sensor capable of effectively detecting heavy metals, particularly lead ions. Detection of lead poisoning in its early stages and the ongoing monitoring of lead levels can effectively mitigate direct exposure and associated health risks. Consequently, there is a pressing necessity for the timely identification of lead contamination. In our research, we aim to devise a swift sensor methodology for the real-time assessment of lead concentrations in drinking water.

Materials and Methods.

Preparation of Nano Cobalt complex

The synthesis of the Nano cobalt complex involved several steps. First, a hot ethanolic solution containing the Schiff base ligand (Fig 1) was prepared at 60°C [20, 21]. The Schiff base ligand (0.1 g, 0.314 mmol) was dissolved in ethanol. The amino acid methionine (0.046 g, 0.314 mmol) was dissolved in 15 ml hot distilled water to create the secondary ligand solution. To form the chelates, the hot ethanolic solution of the Schiff base ligand was combined with the methionine solution in distilled water. Then, a hot ethanoic solution containing the cobalt (II) chloride salt (CoCl2.6H2O, 0.314 mmol) was gradually added dropwise to the ligand mixture. This resulting solution was refluxed for 4 hours with continuous stirring. After reflux, the complex began to precipitate out of solution (Fig 2). The sediments were collected via filtration, washed thoroughly, and dried under vacuum over anhydrous calcium chloride. The complex was purified by recrystallization. During this process, the color transformed from orange to dark brown. Finally, the formed complex underwent ultrasonic probe treatment for 10 minutes [22].



Fig 1. Synthesis pathway of the Schiff base ligand (LAMS).

ÇH3



Schiff base Co(II) Compley [(LAMS)(LMET)Co(Cl)].3H2O

Fig 2. Synthesis pathway of the Schiff base Co (II) Complex.

Instrumentation.

Various analytical instruments and techniques were employed to characterize materials and investigate their properties. The CHNS-932 elemental analyzer was utilized to determine the carbon, hydrogen, and nitrogen content [23]. Melting points were assessed using the triforce XMTD-3000 apparatus [24]. Fourier transform infrared (FT-IR) spectra were generated using a Perkin-Elmer 1650 spectrometer with KBr disks [25]. The molar conductance of complex solutions in DMSO was measured using a Jenway 4010 conductivity meter [26, 27, 28]. Mass spectra were obtained via electron ionization at 70 eV on an MS-5988 mass spectrometer [26, 29, 30]. UV-Vis absorption spectra were recorded using a Perkin-Elmer spectrophotometer [31]. Antimicrobial studies were conducted at the Microanalytical Center, while cytotoxicity testing took place at the National Cancer Institute, both at Cairo University [32, 33]. To characterize Nano Cobalt complexes, particle size and surface charge were analyzed using a Nano Sight NS500[34]. After sample degassing, BET surface area and pore volume were determined with a Nova Touch 4L surface area and pore volume analyzer [35]. AFM with an Oxford Jupiter XR was used to examine morphology [36]. Nanoparticles underwent sonication before TEM imaging. Thin films were synthesized via spin coating with a Laurell-650Sz coater under vacuum, and AFM was employed to image the films and measure roughness using a goldtipped probe. Wettability was assessed using the sessile drop method with a Biolin Scientific T200 contact angle analyzer [37]. QCM Nano sensors were fabricated by attaching cobalt complex nanoparticles to gold electrode quartz chips, with gold cleaning and baseline measurements taken before nanoparticle immobilization [38, 39] Fig 3. Cobalt complex nanoparticles have flowed over the sensors at a controlled rate.



Fig 3. Experimental Setup for QCM Assessment of Lead Detection Using Qsenses QCM System.

Establishing of QCM-Based Nano Schiff base cobalt complex

The study used a QCM sensor including an AT-cut quartz crystal chip with a 12 mm diameter gold electrode that resonated at 5 MHz (Q-Sense, Shenzhen, China) [40]. Before the nanomaterial stabilization process, the gold sensor underwent a comprehensive cleaning procedure. The object was submerged in a solution containing aqueous ammonia, H2O2, and doubledistilled water in a volumetric ratio of 5:1:1. The cleaning solution was kept at a temperature of 75°C, and the gold sensor was immersed for 10 minutes. The sensor was washed with double-distilled water and ethanol before being air-dried at ambient temperature. The dehydrated quartz crystal fragment was meticulously placed into the Q-Sense device. A stream of doubledistilled water was first put over the electrode to serve as a background electrolyte. This step was taken to set baseline readings before adding the sensor's nanomaterials. The double-distilled water continuously flowed in the QCM module until the QCM signal stabilized; at this point, the signal value was zero. After the baseline measurement, a solution was generated by combining 2 mL of 1 ppm Nano ternary Schiff base cobalt complex nanoparticles with 10 mL of double-distilled water. After that, the blend was added to the gold sensor at a flow rate of 0.4 mL/min [34, 41, 42].

QCM-Monitoring of Lead ions.

Quartz crystal microbalance (QCM) experiments were performed using a commercial QCM system to monitor the binding of lead ions to the cobalt complex nanoparticle sensors [41] Fig 3. The measurements involved injecting 1 ppm lead solutions over the Nano sensor-coated QCM chips at controlled temperatures (20°C, 25°C, and 30°C) [43, 44] and pH values (3.5, 7, and 11) [45]. The lead solution was injected repeatedly until the sensor response stabilized, indicating that binding equilibrium was reached. After a set time, double-distilled water was flushed through the QCM module to remove any unbound lead and regenerate the sensor surface for subsequent measurements. This process provided insights into the interaction between the nanoparticle sensors and lead ions under different condition

Results and Discussion

Characterization of nanoparticles of cobalt Schiff base Quinazoline complex

The Nano Cobalt complex has a unique chemical composition and notable biological properties. It is air-stable and can easily dissolve in polar organic solvents such as Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). However, it is insoluble in water and ethanol. Elemental analysis confirms this complex's 1:1:1 Metal to Ligand 1 to Ligand 2 (M: LAMS: LMET) ratio [The Calculated for (C23H34CoClN705S) was C: 44.91%, H: 5.57%, N: 15.94%, S: 5.21%, Cl: 5.76%, Co: 9.58%. While the actual values found are: C: 44.81%, H: 5.44%, N: 15.77%, S: 5.21%, Cl: 5.62%, Co: 9.41%]. Its molar conductivity (Am) in DMSO (at a concentration of 10–3 M) at 25 °C is 17 Ω –1 mol–1 cm2, indicating its non-electrolyte nature [46]. The coordination mechanism of this hybrid ligand to the cobalt center can be elucidated by comparing the infrared spectra of the parent Schiff base ligand and Schiff base Quinazoline complex. The IR spectrum of (LAMS) has a significant peak at 1605 and 1545 cm-1, attributed to (C=N) azomethine and (C=N) pyridine, respectively (Fig 4A) [47, 48]. In the metal complex (Fig 4B), these peaks shifted to higher wavenumbers: 1629 and 1565 cm-1, respectively [49]. Moreover, a broad vibration band associated with the v (N-H) was observed at 3437 cm-1, indicating the stretching vibration of the coordinated water molecule's N-H bonds [50]. This alteration strongly implies the involvement of (C=N) groups in coordination. Two other characteristic bands were observed at 1426, 1340 cm-1 linked to (COO-)asy and (COO-)sym, indicating the Methionine ligand's carboxylic group's involvement in coordination with the metal ions [51, 52]. Furthermore, the characteristic band v (CH2-S) of methionine remains unaltered. Non-ligand bands in the 476 cm-1 and 565 cm-1 range correspond to v(M-N) and v(M-O), respectively [53, 54, 55]. Based on this data, the suggested formula for the cobalt complex is [(LAMS)(LMET)Co(Cl)].3H2O. In the UV-Vis spectrum, the cobalt complex exhibited peaks at 290 nm, 294 nm, and 296 nm, indicating π - π * conjugated systems, while a peak at 334 nm predicted n- π * transitions. Furthermore, a peak at 357 nm revealed a charge transfer [56, 57, 58]. The ESI-MS technique confirmed the cobalt complex shown at m/z =616.10 [M+1]+, while the calculated m/z value equals 615.02. The Schiff base ligand (LAMS) moiety at 318.78 m/z and the Methionine (LMET) moiety at 149 m/z strongly indicate the occurrence of the complexation process. From the ESI-MS results, the molecular ions confirm the 1:1:1 stoichiometric ratio for metal to ligand (LAMS) to ligand (LMET). Thermal analysis of the [(LAMS)(LMET)Co(Cl)].3H2O characterized by the chemical formula (C23H34CoClN7O5S) showed that the first decomposition step took place within the range of $35-110^{\circ}$ C, with a peak observed at 80° C, signifying the loss of three hydrated water molecules. This accounted for an estimated mass loss of 8.63% (calculated = 8.70%). The subsequent step occurred from 110-545°C with a peak at 270°C, involving the loss of C13H21CIN2OS, resulting in an estimated mass loss of 47.50% (calculated = 47.50%). The final step, spanning 545-800°C with a peak at 575°C, indicated the loss of C10H7N5, leading to an estimated mass loss of 31.70% (calculated = 32.07%). This left behind cobalt oxide (CoO) as the decomposition product. Regarding its biological activity, the cobalt complex's antibacterial and antifungal properties were assessed using the disc diffusion method [59]. The complex displayed moderate efficacy against Gram-negative bacteria (Klebsiella Pneumonia) with a diameter of 12.3±0.5mm and no efficacy against Gram-negative bacterium (Escherichia coli) compared to the standard Gentamicin antibiotic. For gram-positive bacteria, it has moderate activity against Staphylococcus Aureus (ATCC: 13565) with an inhibition zone diameter of 18.3±0.5 mm and no activity against Streptococcus mutans (ATCC: 25175) compared to the standard Ampicillin antibiotic. It also possesses high antifungal activity against Candida Albicans (ATCC: 10231) with an inhibition zone diameter of 18.3±0.5 mm and Aspergillus Nigar (ATCC: 16404) with an inhibition zone diameter of 16.3±0.6 compared to the standard antibiotic Nystatin.



Fig 4. IR spectra of (A) Schiff base Quinazoline ligand (L1) and (B) its cobalt (II) complex [(LAMS)(LMET)Co(Cl)].3H2O

XRD

Recent a dvances in powder X-ray diffraction (XRD) have enhanced the ability to investigate the physicochemical makeup of unknown materials. XRD remains a prevalent technique for determining unit cell dimensions and symmetry, providing qualitative, quantitative, and other analytical information [60, 61]. The translation symmetry and unit cell features can be deduced from the peak positions in the diffraction pattern. The size and shape of the unit cell can be elucidated by identifying several Bragg reflections. In this case, reflections at 20 values of 25.912°, 27.491°, 10.377°, 17.132°, and 36.810° correspond to the (101), (002), (100), (110), and (112) planes, respectively. These planes indicate a face-centered cubic crystal structure for the Nano cobalt material [62, 63] (Fig. 5). The XRD data is consistent with the Nano Cobalt's primarily cubic morphology with exposed cubic, rectangular, and rhombic crystal faces. The presence of additional peaks related to hexagonal planes also implies the nanoparticles may contain some domains exhibiting a mixed cubic-hexagonal phase character.



Fig 5. Powder X-ray Diffraction Techniques for Studying Material Composition of the New Synthesized Quinazoline Nano cobalt Complex.

Textural characters (AFM) of Cobalt Complex Nanoparticles.

The surface morphology of the synthesized Nano cobalt complex was closely examined using Atomic force microscopy (AFM) [64]. The AFM images revealed a nonporous, sponge-like structure (Fig. 6), with no visible signs of particle aggregation or agglomeration. Analysis of the AFM data indicated that the nanoparticle size was below 53 nm.



Fig 6. (A) Two-dimensional AFM Visualization and (B) Three-dimensional AFM Image of the Nano Cobalt Schiff Base Complex.

DLS and Zeta Potential

The nanoparticle size distribution and colloidal stability of the synthesized Nano cobalt complex were evaluated using Dynamic Light Scattering (DLS) analysis [65]. The results revealed that the Nano cobalt complex had an average particle size of 24.363 nm Fig 7 (A), exhibiting a uniform size distribution with a low polydispersity index. This low polydispersity index indicates that the Nano cobalt complex suspension possesses remarkable colloidal stability and uniformity in particle size distribution. Furthermore, the zeta potential measurement of the Nano cobalt complex was found to be -16.1 Mv Fig 7 (B). The zeta potential value is a crucial parameter that reflects the physicochemical stability of nanoparticles during storage and handling [66]. A higher absolute value of zeta potential generally corresponds to greater overall system stability, as it indicates stronger repulsive forces between the nanoparticles, preventing their agglomeration [67]. The obtained results, including the narrow particle size distribution and the moderately negative zeta potential value, suggest that the synthesized Nano cobalt complex possesses exceptional colloidal stability and uniform dispersion characteristics [68, 69]. These properties are highly desirable for various applications involving nanoparticles, as they ensure consistent performance and prolonged stability during storage and utilization.



Fig 7. (A) Particle Size Distribution and (B) Zeta Potential Analysis of Nano Cobalt Complex.

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 [70]. In the study of the Nano Schiff base cobalt 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 [71, 72, 73]. Notably, each sample of cobalt complex nanoparticles exhibited type IV nitrogen adsorption-desorption isotherms with hysteresis loops, confirming their macroporous nature [74, 75]. The multipoint BET surface area (Fig. 8) was found to be 50.7563 m²/g, with an Average Particle radius of 2.6866e+001 nm and an Average Pore Size of 8.3408 nm. This significant multipoint BET surface area enhances the capacity of metal complex nanoparticles to adsorb Lead ions in aqueous solutions [76, 77]. The presence of macroporous structure enhances the adsorption of Lead ions on the surface of the metal complex nanoparticles.



Fig 8. Illustrates the N2-isotherm of the Nano Co(II) complex. Contact angle, Hydrophobicity, and toxicity of cobalt Nano complex

The Nano Cobalt complex particles displayed hydrophobic properties, demonstrated by a significant water contact angle measuring 121.59° Fig. 9(A) [78, 79, 80]. This inherent hydrophobic nature expands the potential applications of these nanoparticles as effective sensors in aqueous settings. Ensuring the material's non-toxicity is crucial in the quest for eco-friendly nanoparticle-based sensors. A thorough evaluation of the cytotoxicity of the Nano cobalt complex revealed a reassuring IC50 value of 587.57 µg/ml Fig. 9(B) [81, 82]. This notably high IC50 value promotes the adoption of the Nano cobalt complex as a sensor for water-related applications.



Fig 9 : (A) Hydrophobic and (B) Non-Toxic Properties of Nano Cobalt Complex Particles. Quartz Crystal Microbalance (QCM) Analysis of Lead Ion Detection by Nano Cobalt Complex Sensor.

The performance of a Nano Cobalt complex sensor in detecting lead ions can be evaluated using a Quartz Crystal Microbalance (QCM) analysis, which can be divided into four distinct stages [34, 35, 83, 84]:

A. Baseline Stability: Initially, the sensor's frequency response is recorded to establish a stable baseline, serving as a reference for subsequent stages.

B. Rapid Frequency Drop: Upon exposure to lead ions, a sudden and significant decrease in frequency is observed due to the swift binding of lead ions to the numerous vacant sites on the sensor's surface.

C. Continued Adsorption: As the experiment progresses, further adsorption of lead ion molecules takes place on the Nano Cobalt complex sensor's surface, demonstrating its ability to capture additional lead ions.

D. Equilibrium State: Eventually, an equilibrium state is reached in the adsorption process between the Nano Cobalt complex and lead ion molecules. At this stage, the sensor's frequency shift stabilizes, indicating that the maximum capacity for lead ion adsorption has been reached.

The accompanying figure (2, 7, 8) illustrates the sensor's performance throughout these stages, showcasing its capacity to effectively bind lead ions. Once the frequency stabilizes again, it signifies the attainment of an equilibrium state in the adsorption of lead ions on the QCM-based cobalt complex nanosensor's surface. At this fourth stage, minimal mass loss and minor structural modifications to the nanosensor's surface are observed, reaffirming its effectiveness in lead ion detection.

Proposed Sensing Mechanism of the QCM-Based Nano Cobalt Complex

The lower electronegativity of lead ions compared to the nano cobalt sensor facilitates various types of interactions, contributing to the sensor's effectiveness in lead ion detection. The key interaction mechanisms include:

A. Dipole-dipole interactions: Due to the electronegativity difference, dipole-dipole interactions arise between the Nano Cobalt sensor and lead ions.

B. π - π interactions: The presence of aromatic systems in the Nano Cobalt complex allows for π - π interactions with lead ions.

C. Electrostatic interactions: The polar side chains in the Nano Cobalt complex, acting as functional groups with electrondonating properties, create a negative charge density on the sensor's surface. This negative charge density promotes electrostatic interactions with the positively charged lead ions.

The combination of dipole-dipole interactions, π - π interactions, and strong electrostatic interactions, facilitated by the lower electronegativity of lead ions, enhances the interaction between the QCM-based Nano Cobalt sensor and lead ions [85]. This synergistic effect contributes to the sensor's heightened propensity for lead ion binding and detection, as demonstrated by the QCM analysis.

Effect of temperature

The provided graph illustrates the influence of temperature on the frequency shift (Δ f) of Nano Cobalt (II) Schiff base complexes in response to lead ion solutions. The frequency shift observed in a quartz crystal microbalance (QCM) system is directly proportional to the mass change on the sensor surface, allowing for the detection and quantification of adsorbed lead ions. The graph (Fig 10) displays the frequency shift curves at three different temperatures: 20°C, 25°C, and 30°C. The temperature plays a crucial role in the adsorption process and the subsequent detection of heavy metal ions, such as lead, onto the Nano Cobalt(II) Schiff base complex adsorbent. At 20°C, the frequency shift curve shows a relatively gradual decrease, indicating a slower adsorption rate of lead ions onto the adsorbent surface. Lower temperatures generally result in reduced kinetic energy of the metal ion and adsorbent particles, leading to fewer collisions and a slower adsorption process [86]. As the temperature increases to 25°C, the frequency shift curve exhibits a more pronounced decrease compared to 20°C, suggesting an enhanced adsorption rate. The higher kinetic energy of the particles at this temperature facilitates more frequent collisions and improves the diffusion of lead ions onto the adsorbent's surface [87]. At 30°C, the frequency shift curve displays the most significant decrease, indicating the highest adsorption rate of lead ions onto the Nano Cobalt (II) Schiff base complex. The increased temperature further enhances the kinetic energy of the particles, leading to more effective collisions and improved mass transfer of lead ions to the adsorbent's surface [3]. The observed temperature effect on the adsorption of lead ions onto Nano Cobalt (II) Schiff base complexes can be attributed to several factors, including:

- 1. Increased kinetic energy and mobility of the adsorbate (lead ions) and adsorbent particles at higher temperatures, leading to more frequent collisions and improved mass transfer [88].
- 2. Enhanced diffusion rates of lead ions through the boundary layer and within the pores of the adsorbent at higher temperatures [89, 90].
- 3. Potential changes in the adsorbent's surface properties and functional groups may affect the adsorption affinity and capacity [91].
- 4. The Influence of temperature on the speciation and solubility of lead ions in aqueous solutions can impact their availability for adsorption [92].

It is important to note that while higher temperatures generally promote adsorption kinetics, excessive temperatures may also lead to desorption or degradation of the adsorbent material, potentially reducing its adsorption capacity [93]. Therefore, an optimal temperature range should be determined for each specific adsorbent-adsorbate system.



Fig 10. Impact of Temperature on Sensitivity of Nano Schiff base Cobalt complex in Detecting Lead ions.

Effect of pH

The provided graph (Fig 11) illustrates the frequency shift (Δf) of Nano Cobalt (II) Schiff base complexes in response to lead ion solutions at different pH values, specifically 3.5, 7, and 11. The frequency shift in a quartz crystal microbalance (OCM) system is directly proportional to the mass change on the sensor surface, allowing for the detection and quantification of adsorbed lead ions [94, 95]. At a pH of 3.5, the curve shows a rapid and substantial decrease in frequency, indicating significant adsorption of lead ions onto the Nano Cobalt (II) Schiff base complex. This can be attributed to the predominance of free lead cations (Pb2+) in the solution at low pH values, which can effectively interact with the negatively charged functional groups on the adsorbent's surface through electrostatic attractions. As the pH increases to 7 (neutral conditions), the frequency shift curve exhibits a less pronounced decrease compared to pH 3.5. This suggests a reduced adsorption efficiency of lead ions onto the Nano Cobalt (II) Schiff base complex. At this pH, lead ions may form various hydroxide complexes or precipitates, reducing their availability for adsorption. Additionally, the surface charge of the adsorbent may be altered, affecting the electrostatic interactions. At a pH of 11 (alkaline conditions), the frequency shift curve shows a relatively small decrease, indicating minimal adsorption of lead ions onto the Nano Cobalt (II) Schiff base complex. In highly alkaline environments, lead ions tend to form insoluble hydroxide precipitates, significantly reducing their availability for adsorption. Furthermore, the surface of the adsorbent may become highly negatively charged, leading to repulsive forces that hinder the adsorption process. These observations highlight the crucial role of pH in the adsorption of lead ions onto Nano Cobalt (II) Schiff base complexes for QCM-based detection. The optimal pH condition for lead ion adsorption appears to be acidic (pH 3.5), where the lead cations are readily available, and the electrostatic interactions between the adsorbent and lead ions are favoured. It is worth noting that the pH effect on adsorption depends not solely on the metal ion speciation but also on the ionization state of functional groups on the adsorbent's surface [96, 97]. The Nano Cobalt (II) Schiff base complex likely possesses functional groups that undergo protonation or deprotonation reactions depending on the pH, influencing the overall surface charge and adsorption behaviour. By understanding the pH effect on the adsorption of lead ions onto Nano Cobalt (II) Schiff base complexes, researchers can optimize the QCM-based detection method for heavy metals like lead in various applications, such as environmental monitoring, industrial effluent treatment, and water purification



Fig 11. Imaging reveals the impact of pH of Lead ions solution on the performance of QCM sensor based on Nano Schiff base Cobalt complex. Conclusion

223

This research presented the synthesis, characterization, and application of a novel Nano Cobalt(II) Schiff base complex for detecting lead ions in water using a quartz crystal microbalance (QCM) sensor. The Nano Cobalt complex was thoroughly characterized using various analytical techniques like FT-IR, UV-Vis, mass spectrometry, and thermal analysis to confirm its molecular structure. Textural characterization methods such as XRD, AFM, DLS, zeta potential, BET surface area, and contact angle measurements provided insight into the nanoscale morphology, particle size, surface properties, and complex porosity. The QCM sensor fabricated using the nano cobalt complex demonstrated rapid and sensitive detection of lead ions in aqueous solutions. The adsorption and detection performance were studied under varying pH and temperature conditions. At a lower pH of around 3.5 and higher temperatures of around 30°C, the sensor exhibited enhanced adsorption and detection of lead ions, which were attributed to favorable electrostatic interactions and increased kinetics. Overall, the developed nano cobalt Schiff base complex-based QCM sensor shows promising potential for real-time monitoring of lead contamination in water resources with high sensitivity and fast response time, addressing an important environmental and health concern. The synergistic combination of the nano-structured complex and QCM transduction mechanism enables efficient lead ion sensing for water quality assessment.

References

- [1]R. Lutyński, "The role of lead as an environmental pollutant in the period of growing ecological consciousness.," Przegl. Lek., vol. 53, no. 4, pp. 371-374, 1996.
- [2]A. Violante, V. Cozzolino, L. Perelomov, A. G. Caporale, and M. Pigna, "Mobility and bioavailability of heavy metals and metalloids in soil environments," J. soil Sci. plant Nutr., vol. 10, no. 3, pp. 268-292, 2010.
- [3]J. E. Gall, R. S. Boyd, and N. Rajakaruna, "Transfer of heavy metals through terrestrial food webs: a review," Environ. Monit. Assess., vol. 187, pp. 1-21, 2015.
- [4]J. Singh and A. S. Kalamdhad, "Effects of heavy metals on soil, plants, human health and aquatic life," Int J Res Chem Env., vol. 1, no. 2, pp. 15-21, 2011.
- [5]T. A. Jusko, C. R. Henderson Jr, B. P. Lanphear, D. A. Cory-Slechta, P. J. Parsons, and R. L. Canfield, "Blood lead concentrations< 10 µg/dL and child intelligence at 6 years of age," Environ. Health Perspect., vol. 116, no. 2, pp. 243-248, 2008.
- [6]H. Abadin, A. Ashizawa, F. Llados, and Y.-W. Stevens, "Toxicological profile for lead," 2007.
- [7]S. J. S. Flora, G. Flora, and G. Saxena, "Environmental occurrence, health effects and management of lead poisoning," in Lead, Elsevier, 2006, pp. 158-228.
- [8]M. S. Collin et al., "Bioaccumulation of lead (Pb) and its effects on human: A review," J. Hazard. Mater. Adv., vol. 7, p. 100094, 2022.
- [9]R. Liu, J. Cui, T. Ding, Y. Liu, and H. Liang, "Research Progress on the Biological Activities of Metal Complexes Bearing Polycyclic Aromatic Hydrazones," Molecules, vol. 27, no. 23, p. 8393, 2022.
- [10] A. K. El-Sawaf, F. El-Essawy, A. A. Nassar, and E.-S. A. El-Samanody, "Synthesis, spectral, thermal and antimicrobial studies on cobalt (II), nickel (II), copper (II), zinc (II) and palladium (II) complexes containing thiosemicarbazone ligand," J. Mol. Struct., vol. 1157, pp. 381-394, 2018.
- [11] S. M. Kumar et al., "Synthesis, characterization, crystal structure and cytotoxic properties of thiosemicarbazide Ni (II) and Zn (II) complexes," Spectrochim. Acta Part A Mol. Biomol. Spectrosc., vol. 142, pp. 292-302, 2015.
- [12] E. Pahonțu, F. Julea, Y. Chumakov, P. Petrenco, T. Roșu, and A. Gulea, "Synthesis, characterization, crystal structure and antiproliferative activity studies of Cu (II), Ni (II) and Co (II) complexes with 4-benzoyl-5-pyrazolones derived compounds," J. Organomet. Chem., vol. 836, pp. 44–55, 2017.
- [13] N. Bereli, D. Çimen, H. Yavuz, and A. Denizli, "Sensors for the detection of heavy metal contaminants in water and environment," Nanosensors Environ. Food Agric. Vol. 1, pp. 1-21, 2021.
- [14] B. Wu, L. Ga, Y. Wang, and J. Ai, "Recent Advances in the Application of Bionanosensors for the Analysis of Heavy Metals in Aquatic Environments," Molecules, vol. 29, no. 1, p. 34, 2023.
- [15] A. Salek Maghsoudi, S. Hassani, K. Mirnia, and M. Abdollahi, "Recent advances in nanotechnology-based biosensors development for detection of arsenic, lead, mercury, and cadmium," Int. J. Nanomedicine, pp. 803-832, 2021.
- [16] 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.
- [17] N. S. and T. C. (NSTC)., "The National Nanotechnology Initiative: Research and Development Leading to a Revolution in Technology and Industry," A Suppl. to Pres. FY 2006 Budg., 2005.
- [18] T. R. Fadel et al., "Toward the responsible development and commercialization of sensor nanotechnologies," ACS sensors, vol. 1, no. 3, pp. 207–216, 2016. [19] L. Manjakkal et al., "Connected sensors, innovative sensor deployment, and intelligent data analysis for online water
- quality monitoring," IEEE Internet Things J., vol. 8, no. 18, pp. 13805-13824, 2021.
- [20] A. El-Sherif, W. Mahmoud, W. Hosny, and E. Komyha, "Design, Structural characterization, Molecular docking, and biomedical applications of hydrazone -based Schiff base metal complexes," Egypt. J. Chem., vol. 0, no. 0, pp. 0-0, 2023, doi: 10.21608/ejchem.2023.147796.6650.
- [21] A. N. Al-Hakimi, M. N. R. Alotaibi, N. A. Al-Gabri, and J. S. Alnawmasi, "Biological evaluation of nano-sized novel Schiff base ligand-based transition metal complexes," Results Chem., vol. 6, p. 101107, 2023.
- [22] Y. Tang, Development, characterization and applications of electrodes modified with conductive polymers, ionic liquids and proteins. Oakland University, 2009.
- [23] M. Bird, C. Keitel, and W. Meredith, "Analysis of biochars for C, H, N, O and S by elemental analyser," Biochar a Guid. to Anal. methods, vol. 39, 2017.
- [24] H. M. Fahmy, F. M. Abdel-Rahman, A. A. El-Sayed, and A. A. El-Sherif, "Study of novel bidentate heterocyclic amine-based metal complexes and their biological activities: cytotoxicity and antimicrobial activity evaluation," BMC Chem., vol. 17, no. 1, p. 78, 2023.

- [25] O. M. Fahmy, W. H. Mahmoud, R. M. El Nashar, and A. A. El-Sherif, "Nano Co (II) and Pd (II) Schiff base Complexes: Structural Characterization, Molecular docking, Antitumor proficiency and Biological evaluation," Egypt. J. Chem., vol. 66, no. 13, pp. 1373–1382, 2023.
- [26] W. H. Mahmoud, M. Bayomi, M. ElMosallamy, and A. A. El-Sherif, "Schiff base transition metal (II) complexes: spectral analyses and biological application," Egypt. J. Chem., vol. 67, no. 3, pp. 379–386, 2024.
- [27] A. M. Alsuhaibani, A. M. A. Adam, M. S. Refat, M. I. Kobeasy, S. B. Bakare, and E. S. Bushara, "Spectroscopic, thermal, and anticancer investigations of new cobalt (II) and nickel (II) triazine complexes," Bull. Chem. Soc. Ethiop., vol. 37, no. 5, pp. 1151–1162, 2023.
- [28] S. M. El-Megharbel, S. H. Qahl, K. Althobaiti, E. H. A.-T. H. Al, and R. Z. Hamza, "Antioxidant novel activities of curcumin complexes with Mg (II), Ca (II), Cu (II), Cr (III) and Se (IV) metal ions: synthesis and spectral studies," Bull. Chem. Soc. Ethiop., vol. 38, no. 2, pp. 347–363, 2024.
- [29] E. M. Komyha, W. H. Mahmoud, W. M. Hosny, and A. A. El-Sherif, "Design, Structural Characterization, Molecular docking and Biomedical Applications Of Hydrazone-based Schiff base Metal Complexes," Egypt. J. Chem., vol. 66, no. 13, pp. 1219–1230, 2023.
- [30] N. H. Mahmoud, H. S. Magar, M. G. Rizk, and A. M. Fahim, "Comparative, Synthesis, ADME studies, and Electrochemical studies, of the divalent and monovalent binuclear complexes of malonate derivatives," J. Mol. Struct., p. 137717, 2024.
- [31] H.-H. Perkampus, UV-VIS Spectroscopy and its Applications. Springer Science & Business Media, 2013.
- [32] M. A. Hosny, Y. H. Zaki, W. A. Mokbel, and A. O. Abdelhamid, "Synthesis, characterization, antimicrobial activity and anticancer of some new pyrazolo [1, 5-a] pyrimidines and pyrazolo [5, 1-c] 1, 2, 4-triazines," Med. Chem. (Los. Angeles)., vol. 16, no. 6, pp. 750–760, 2020.
- [33] A. M. Naglah et al., "Nα-1, 3-benzenedicarbonyl-bis-(Amino acid) and dipeptide candidates: synthesis, cytotoxic, antimicrobial and molecular docking investigation," Drug Des. Devel. Ther., pp. 1315–1332, 2021.
- [34] W. Al-Gethami, D. Alhashmialameer, N. Al-Qasmi, 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.
- [35] N. Al-Qasmi, W. Al-Gethami, D. Alhashmialameer, S. H. Ismail, and A. H. Sadek, "Evaluation of green-synthesized cuprospinel nanoparticles as a nanosensor for detection of low-concentration Cd (II) ion in the aqueous solutions by the quartz crystal microbalance method," Materials (Basel)., vol. 15, no. 18, p. 6240, 2022.
- [36] J. Ji, S. Mazinani, E. Ahmed, Y. M. J. Chew, and D. Mattia, "Hydrophobic poly (vinylidene fluoride)/siloxene nanofiltration membranes," J. Memb. Sci., vol. 635, p. 119447, 2021.
 [37] T. Dey and D. Naughton, "Cheap non-toxic non-corrosive method of glass cleaning evaluated by contact angle, AFM,
- [37] T. Dey and D. Naughton, "Cheap non-toxic non-corrosive method of glass cleaning evaluated by contact angle, AFM, and SEM-EDX measurements," Environ. Sci. Pollut. Res., vol. 24, pp. 13373–13383, 2017.
- [38] A. G. G. C. Premaratne, "Electrochemical and Surface Plasmon Bioassays for Circulating Biomarkers." Oklahoma State University, 2018.
- [39] R. Sinha, S. Dwivedi, A. Kumar, and P. Srivastava, "Materials in bio-sensing of water pollutants," Sensors Water Pollut. Monit. Role Mater., pp. 187–211, 2020.
- [40] Available: https://www.biolinscientific.com/qsense.
- [41] Q. Zhang et al., "QCM-nanomagnetic beads biosensor for lead ion detection," Analyst, vol. 143, no. 2, pp. 549–554, 2018.
- [42] Q. Chen, S. Xu, Q. Liu, J. Masliyah, and Z. Xu, "QCM-D study of nanoparticle interactions," Adv. Colloid Interface Sci., vol. 233, pp. 94–114, 2016.
- [43] C. Song, Z. Ma, C. Li, H. Zhang, Z. Zhu, and J. Wang, "Application of Heat-Enhancement for Improving the Sensitivity of Quartz Crystal Microbalance," Biosensors, vol. 12, no. 8, p. 643, 2022.
- [44] J. J. Hamon, A. Striolo, and B. P. Grady, "Observing the Effects of Temperature and Surface Roughness on Cetyltrimethylammonium Bromide Adsorption Using a Quartz-Crystal Microbalance with Dissipation Monitoring," J. Surfactants Deterg., vol. 22, no. 5, pp. 1201–1212, 2019.
- [45] W. H. Mahmoud, A. A. Fayek, A. Taha, and A. A. El-Sherif, "Synthesis, textural and thermal properties of Nano super hydrophobic cupper complex as QCM based dye sensor," Egypt. J. Chem., 2023.
- [46] M. Hanif and Z. H. Chohan, "Design, spectral characterization and biological studies of transition metal (II) complexes with triazole Schiff bases," Spectrochim. Acta Part A Mol. Biomol. Spectrosc., vol. 104, pp. 468–476, 2013.
- [47] W. Rehman, R. Yasmeen, F. Rahim, and M. Waseem, "CY, Guo, Z. Hassa, U. Rashid, K," J Photochem. Photobiol., B Biol., vol. 164, p. 65, 2016.
- [48] E. Ghasemi Gorji, N. Monadi, and M. Mohseni, "Synthesis, characterization and antibacterial activities of Mo (VI) and Cu (II) complexes derived from tridentate ONO Schiff base ligands," Appl. Chem., vol. 11, no. 41, pp. 119–128, 2016.
- [49] K. Mohammadi, S. S. Azad, and A. Amoozegar, "New tetradentate Schiff bases of 2-amino-3, 5-dibromobenzaldehyde with aliphatic diamines and their metal complexes: Synthesis, characterization and thermal stability," Spectrochim. Acta Part A Mol. Biomol. Spectrosc., vol. 146, pp. 221–227, 2015.
- [50] M. Anu, L. Prabha, G. Banukarthi, P. R. Kanjana, and K. Rajeswari, "UV-visible, IR and NMR spectra on Copper (II) Schiff base Complex," Int. J. Institutional Pharm. Life Sci., vol. 3, no. 6, pp. 23–32, 2013.
- [51] B. K. Singh, H. K. Rajour, and A. Prakash, "Synthesis, characterization and biological activity of transition metal complexes with Schiff bases derived from 2-nitrobenzaldehyde with glycine and methionine," Spectrochim. Acta Part A Mol. Biomol. Spectrosc., vol. 94, pp. 143–151, 2012.
- [52] M. A. Mamun, O. Ahmed, P. K. Bakshi, and M. Q. Ehsan, "Synthesis and spectroscopic, magnetic and cyclic voltammetric characterization of some metal complexes of methionine:[(C5H10NO2S) 2MII]; MII= Mn (II), Co (II), Ni (II), Cu (II), Cd (II) and Hg (II)," J. Saudi Chem. Soc., vol. 14, no. 1, pp. 23–31, 2010.
- [53] K. D. Patel and H. S. Patel, "Synthesis, spectroscopic characterization and thermal studies of some divalent transition metal complexes of 8-hydroxyquinoline," Arab. J. Chem., vol. 10, pp. S1328–S1335, 2017.
- [54] L. Bellamy, The infra-red spectra of complex molecules. Springer Science & Business Media, 2013.

- [55] K. Mohammadi, S. S. Azad, and A. Amoozegar, "New tetradentate Schiff bases of 2-amino-3, 5-dibromobenzaldehyde with aliphatic diamines and their metal complexes: Synthesis, characterization and thermal stability," Spectrochim. Acta Part A Mol. Biomol. Spectrosc., vol. 146, pp. 221–227, 2015.
- [56] S. İlhan, "Synthesis and spectral studies of new macrocyclic Schiff base Cu (II), Ni (II), Cd (II), Zn (II), Pb (II), and La (III) complexes containing pyridine head unit," Russ. J. Coord. Chem., vol. 35, no. 5, pp. 347–351, 2009.
- [57] A. A. Abou-Hussein and W. Linert, "Synthesis, spectroscopic, coordination and biological activities of some organometallic complexes derived from thio-Schiff base ligands," Spectrochim. Acta Part A Mol. Biomol. Spectrosc., vol. 117, pp. 763–771, 2014.
- [58] M. A. Arafath, F. Adam, M. R. Razali, L. E. A. Hassan, M. B. K. Ahamed, and A. M. S. A. Majid, "Synthesis, characterization and anticancer studies of Ni (II), Pd (II) and Pt (II) complexes with Schiff base derived from Nmethylhydrazinecarbothioamide and 2-hydroxy-5-methoxy-3-nitrobenzaldehyde," J. Mol. Struct., vol. 1130, pp. 791– 798, 2017.
- [59] A. Bauer, W. M. M. Kirby, and J. C. Sherris, "turck, Turck M. Antibiotic susceptibility testing by a standardized single disk method," Am. J. Clin. Pathol., vol. 45, no. 4, p. 493, 1966.
- [60] A. L. Patterson, "The Scherrer formula for X-ray particle size determination," Phys. Rev., vol. 56, no. 10, p. 978, 1939.
- [61] H. E. Swanson, Standard X-ray diffraction powder patterns, vol. 25. US Department of Commerce, National Bureau of Standards, 1953.
- [62] S. Mourdikoudis, R. M. Pallares, and N. T. K. Thanh, "Characterization techniques for nanoparticles: comparison and complementarity upon studying nanoparticle properties," Nanoscale, vol. 10, no. 27, pp. 12871–12934, 2018.
- [63] B. S. Murty and S. Ranganathan, "Novel materials synthesis by mechanical alloying/milling," Int. Mater. Rev., vol. 43, no. 3, pp. 101–141, 1998.
- [64] L. Angeloni, D. Passeri, P. G. Schiavi, F. Pagnanelli, and M. Rossi, "Magnetic force microscopy characterization of cobalt nanoparticles: A preliminary study," in AIP Conference Proceedings, AIP Publishing, 2020.
- [65] S. M. Ansari et al., "Cobalt nanoparticles for biomedical applications: Facile synthesis, physiochemical characterization, cytotoxicity behavior and biocompatibility," Appl. Surf. Sci., vol. 414, pp. 171–187, 2017.
- [66] S. Bhattacharjee, "DLS and zeta potential-what they are and what they are not?," J. Control. release, vol. 235, pp. 337– 351, 2016.
- [67] J. Jiang, G. Oberdörster, and P. Biswas, "Characterization of size, surface charge, and agglomeration state of nanoparticle dispersions for toxicological studies," J. Nanoparticle Res., vol. 11, pp. 77–89, 2009.
- [68] H. Takeuchi, H. Yamamoto, and Y. Kawashima, "Mucoadhesive nanoparticulate systems for peptide drug delivery," Adv. Drug Deliv. Rev., vol. 47, no. 1, pp. 39–54, 2001.
- [69] K. Fernández, J. Aburto, C. von Plessing, M. Rockel, and E. Aspé, "Factorial design optimization and characterization of poly-lactic acid (PLA) nanoparticle formation for the delivery of grape extracts," Food Chem., vol. 207, pp. 75–85, 2016.
- [70] M. Thommes, K. Kaneko, A. V Neimark, and J. P. Olivier, "FR-R., & Sing, JR and KSW (2013). Brunauer-Emmett-Teller (BET) surface area analysis," Pure Appl. Chem., vol. 87, no. 9–10, pp. 1051–1069.
- [71] F. A. L. Dullien and V. K. Batra, "Determination of the structure of porous media," Ind. Eng. Chem., vol. 62, no. 10, pp. 25–53, 1970.
- [72] Y. Tian, Q. Chen, C. Yan, H. Deng, and Y. He, "Classification of adsorption isotherm curves for shale based on pore structure," Petrophysics, vol. 61, no. 05, pp. 417–433, 2020.
- [73] P. Van Der Voort, K. Leus, and E. De Canck, Introduction to porous materials. John Wiley & Sons, 2019.
- [74] Z. Gao et al., "Cobalt nanoparticles packaged into nitrogen-doped porous carbon derived from metal-organic framework nanocrystals for hydrogen production by hydrolysis of sodium borohydride," Int. J. Hydrogen Energy, vol. 44, no. 16, pp. 8365–8375, 2019.
- [75] Y. Wei, Z. Zhao, T. Li, J. Liu, A. Duan, and G. Jiang, "The novel catalysts of truncated polyhedron Pt nanoparticles supported on three-dimensionally ordered macroporous oxides (Mn, Fe, Co, Ni, Cu) with nanoporous walls for soot combustion," Appl. Catal. B Environ., vol. 146, pp. 57–70, 2014.
- [76] W. Fu and Z. Huang, "Magnetic dithiocarbamate functionalized reduced graphene oxide for the removal of Cu (II), Cd (II), Pb (II), and Hg (II) ions from aqueous solution: Synthesis, adsorption, and regeneration," Chemosphere, vol. 209, pp. 449–456, 2018.
- [77] Z. Yang et al., "Effect of aging on chemical and rheological properties of bitumen," Polymers (Basel)., vol. 10, no. 12, p. 1345, 2018.
- [78] F. Golkhou and A. Haghtalab, "Measurement and thermodynamic modeling of carbon dioxide hydrate formation conditions using dry water through hydrophobic nano silica," J. Nat. Gas Sci. Eng., vol. 68, p. 102906, 2019.
- [79] M. Szafraniec and D. Barnat-Hunek, "Evaluation of the contact angle and wettability of hydrophobised lightweight concrete with sawdust," Bud. i Archit., vol. 19, no. 2, 2020.
- [80] S. S. Gavande, Y. H. Navale, A. S. Salunkhe, S. Gavande, P. S. Kulkarni, and B. R. Karche, "Investigation of Supercapacitive Behaviour of Electrodeposited Cobalt Oxide Thin Film by Potentiostatic Mode," J. Nano-and Electron. Phys., vol. 12, no. 2, 2020.
- [81] M. M. Sayed, Z. I. Nabil, N. S. El-Shenawy, R. A. Al-Eisa, and M. S. Nafie, "In Vitro and In Vivo Effects of Synthesis Novel Phenoxyacetamide Derivatives as Potent Apoptotic Inducer against HepG2 Cells through PARP-1 Inhibition," Pharmaceuticals, vol. 16, no. 11, p. 1524, 2023.
- [82] E. T. Nagy et al., "Design and cytotoxic evaluation via apoptotic and antiproliferative activity for novel 11 (4aminophenylamino) neocryptolepine on hepatocellular and colorectal cancer cells," Apoptosis, vol. 28, no. 3–4, pp. 653–668, 2023.
- [83] Z. Yang and C. Zhang, "Designing of MIP-based QCM sensor for the determination of Cu (II) ions in solution," Sensors Actuators B Chem., vol. 142, no. 1, pp. 210–215, 2009.
- [84] M. Yang and J. He, "A copper-manganese composite oxide as QCM sensing layers for detection of formaldehyde gas," RSC Adv., vol. 8, no. 1, pp. 22–27, 2018.

- [85] S. M. M. Hizam, A. M. Al-Dhahebi, and M. S. Mohamed Saheed, "Recent advances in graphene-based nanocomposites for ammonia detection," Polymers (Basel)., vol. 14, no. 23, p. 5125, 2022.
- [86] Q. Yao, J. Xie, J. Liu, H. Kang, and Y. Liu, "Adsorption of lead ions using a modified lignin hydrogel," J. Polym. Res., vol. 21, pp. 1–16, 2014.
- [87] N. A. A. Qasem, R. H. Mohammed, and D. U. Lawal, "Removal of heavy metal ions from wastewater: A comprehensive and critical review," Npj Clean Water, vol. 4, no. 1, p. 36, 2021.
- [88] S. Banerjee and M. C. Chattopadhyaya, "Adsorption characteristics for the removal of a toxic dye, tartrazine from aqueous solutions by a low cost agricultural by-product," Arab. J. Chem., vol. 10, pp. S1629–S1638, 2017. [89] M. R. Hassan and M. I. Aly, "Magnetically synthesized MnFe2O4 nanoparticles as an effective adsorbent for lead ions
- removal from an aqueous solution," AQUA-Water Infrastructure, Ecosyst. Soc., vol. 70, no. 6, pp. 901-920, 2021.
- [90] L. Chaabane, E. Beyou, A. El Ghali, and M. H. V Baouab, "Comparative studies on the adsorption of metal ions from aqueous solutions using various functionalized graphene oxide sheets as supported adsorbents," J. Hazard. Mater., vol. 389, p. 121839, 2020.
- [91] Z. Raji, A. Karim, A. Karam, and S. Khalloufi, "Adsorption of heavy metals: Mechanisms, kinetics, and applications of various adsorbents in wastewater remediation-A review," in Waste, MDPI, 2023, pp. 775-805.
- [92] F. Ergüvenerler, Ş. Targan, and V. N. Tirtom, "Removal of lead from aqueous solutions by low cost and waste biosorbents (lemon, bean and artichoke shells)," Water Sci. Technol., vol. 81, no. 1, pp. 159-169, 2020.
- [93] M. Horsfall Jnr and A. I. Spiff, "Effects of temperature on the sorption of Pb2+ and Cd2+ from aqueous solution by Caladium bicolor (Wild Cocoyam) biomass," Electron. J. Biotechnol., vol. 8, no. 2, pp. 43-50, 2005.
- [94] S. N. A. Mustaffa et al., "Sensing mechanism of an optimized room temperature optical hydrogen gas sensor made of zinc oxide thin films," J. Mater. Res. Technol., vol. 9, no. 5, pp. 10624-10634, 2020.
- [95] D. R. Boverhof and R. M. David, "Nanomaterial characterization: considerations and needs for hazard assessment and safety evaluation," Anal. Bioanal. Chem., vol. 396, pp. 953–961, 2010.
- [96] X. Yang et al., "Surface functional groups of carbon-based adsorbents and their roles in the removal of heavy metals from aqueous solutions: a critical review," Chem. Eng. J., vol. 366, pp. 608-621, 2019.
- [97] M. Onditi, A. A. Adelodun, E. O. Changamu, and J. C. Ngila, "Removal of Pb2+ and Cd2+ from drinking water using polysaccharide extract isolated from cactus pads (Opuntia ficus indica)," J. Appl. Polym. Sci., vol. 133, no. 38, 2016.