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Nano cobalt complex as a highly senstive sensor for detection of methylen blue (MB) by QCM technique

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***ABSTRACT*: The textile industry's dyeing processes generate dyes that act as pollutants, contributing to the discoloration of wastewater and other environmental concerns. These nanosensors hold promise in detecting various azo-toxic dyes present in food products, thereby offering an expansive potential for future innovation in sensor design. Herein explores the advantages of nanosensors over traditional sensing methods, their diverse applications in utilizing nanomaterials, and the potential health consequences of azo dyes on human well-being. The article further outlines critical parameters for determining permissible limits and recommends an Acceptable Daily Intake (ADI) for azo toxic dyes.**

A groundbreaking innovation is a novel nanosensor employing cobalt nanoparticles for detection of Methylene Blue (MB) dye. Characterization of this nano cobalt sensor utilized various analytical tools, including Dynamic Light Scattering (DLS), Zeta potential analysis, Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM), Fourier-Transform Infrared Spectroscopy (FT-IR), as well as BET surface area and pore size determination . Additionally, the sensor's mechanical stability was affirmed through investigation of 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. Impressively, the proposed sensor exhibited rapid and sensitive responses, even at very low dye concentrations (1 ppm), with a swift response time of 3 minutes.

KEYWORDS:* *Nano sensor; nano complex; toxic dyes; TEM

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I. INTRODUCTION

In the realm of sensor development, there exists a pressing need for advancing processing methods to craft specific morphologies and nanostructures in nanomaterials. These nanostructures significantly influence the performance of nanomaterials, underscoring their paramount importance. The integration of nanoscale materials into sensing applications is experiencing a notable expansion, with nanosensors progressively assuming pivotal roles across various sectors. These encompass environmental assessment, pathogen identification, and biomedical diagnostics. The realm of nanomaterial-enabled sensors stands as a captivating technological frontier, enabling remarkably precise detection within the nanomolar to sub-picomolar range for environmental contaminants [1–7].

The allure of these sensors is grounded in their potential to enable effortless, in-field detection of contaminants, obviating the necessity for intricate laboratory apparatus. Nanomaterials have catalyzed breakthroughs in sensor design by enabling miniaturization, enhancing portability, and accelerating signal response times. The strikingly high surface area-to-volume ratios of nanomaterials, coupled with their facile surface modification capabilities, render them exquisitely responsive to alterations in surface chemistry. This unique attribute empowers nanosensors to achieve unprecedentedly low detection thresholds. Notably, in select cases, the heightened

sensitivity of nano-enabled sensors is attributed to the nanomaterials' size similarity to the target analytes (e.g., metal ions, pathogens, biomolecules, antibodies, DNA), enabling exploration of previously inaccessible matrices [8-12].

In our ongoing research endeavors, our primary focus lies in developing an all-encompassing analytical sensor tailored for studying dyes, exemplified by the case of methylene blue dye. The innovative detection system we're developing offers rapid and precise dye determinations with minimal sample preparation or the need for constant instrument supervision

II. MATERIALS AND METHODS

2 1. Preparation of Nano cobalt complex

The synthesis process of the nano cobalt complex involved the combination of a hot ethanolic solution (maintained at 70°C) containing the Schiff base ligand (1 mmol, 0.26 g) Fig [1] with a heated solution of metal salt (0.23 g $CoCl_2 \cdot 6H_2O$) in absolute ethanol (20 ml) [13] . After subjecting the mixture to 3 hours of stirring under reflux conditions, the resulting complex initiated precipitation. These precipitates were carefully gathered via filtration, subsequently washed repeatedly, and finally dried under vacuum conditions using anhydrous calcium chloride [13]. As a result of this systematic process, the metal complex achieved a state of purity through recrystallization. Notably, the ensuing complex underwent a 15-minute treatment with an ultrasonic probe, leading to a distinctive alteration in color – a shift from yellow to a deep brown [13].

Fig. 1. Schiff base ligand (L)

2. Instrumentation.

Microanalysis of carbon, hydrogen, and nitrogen was conducted using a CHNS-932 (LECO) Vario Elemental analyzer at the Microanalytical Center, Cairo University, Egypt [14]. Determination of the melting point was accomplished using the triforce XMTD-3000 apparatus [15]. Fourier transform infrared (FT-IR) spectra were captured employing a Perkin-Elmer 1650 spectrometer, utilizing KBr disks within the spectral range of 4000–400 cm^{-1} [16]. The molar conductance of solid complex solutions in ethanol at concentrations of 10^{-3} M was gauged using a Jenway 4010 conductivity meter [17]. For mass spectra acquisition via the electron ionization method at 70 eV [18], an MS-5988 GS-MS Hewlett-Packard instrument was employed. To generate spectra of solutions spanning wavelengths from 200 to 700 nm [19], a UV-Vis Perkin-Elmer Model Lambda 20 automated spectrophotometer was utilized. The antimicrobial investigation took place at the Microanalytical Center, Cairo University [20], while the assessment of cytotoxic effects was carried out at the National Cancer Institute, Cairo University [21].

To determine the surface charge and particle size of the nano cobalt complex, the zeta potential was assessed using a ZetaSizer instrument (NanoSight NS500, Malvern Panalytical, Malvern, UK) [22]. The surface area and pore volume were quantified using a surface area and pore volume analyzer (Quanta Chrome, Nova Touch 4L, USA) utilizing the BET (Brunauer–Emmett–Teller) multi-point method and the DH (Dubinin-Radushkevich) pore volume method [23]. For the metal complex nanoparticles, a degassing process was performed at 65°C for 1.25 hours.

To gain further insights into the samples, a Transmission Electron Microscope (TEM) instrument (JEOL, JEM-2100 high-resolution, Peabody, MA, USA) was employed [24]. Additionally, Atomic Force Microscopy (AFM) studies were conducted using an AFM instrument manufactured by Oxford company, the Jupiter XR AFM model [25]. This analysis aimed to discern the morphology of the cobalt complex nanoparticles. Prior to TEM analysis, a 15-minute sonication was conducted 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.

The synthesis of thin films was carried out using a Spain coater instrument (Laurell-650Sz, France) under vacuum conditions, with a rotational speed of 750 rpm and a droplet rate of 50 µm per 120 seconds. AFM images and roughness profiles were captured at a size of 47 nm x 47 nm, utilizing a gold-coated cantilever in contact mode with a scanning speed of 0.31 µm/s [26].

For wettability assessment, a Biolin Scientific contact angle analyzer (model T200) was employed. The sessile drop recipe condition was maintained with a measurement time of 10 seconds. A droplet of distilled water (volume: 4 µm) was utilized to determine the surface's wettability [27].

3. Establishing of QCM-Based cobalt complex Nanosensors.

The QCM sensor comprises an AT-cut quartz crystal chip affixed to a gold electrode measuring 12 mm in diameter, boasting a resonance frequency of 5 MHz this instrumentation is sourced from Q-Sense, Shenzhen, China [28].

Before achieving nanomaterial stabilization, the gold sensor underwent a thorough cleaning process. This involved immersing the sensor in a solution consisting of aqueous ammonia, H_2O_2, and double-distilled water

in a 5:1:1 v/v/v ratio. This cleaning solution was maintained at 75°C for 10 minutes. Subsequently, the gold sensor was meticulously rinsed with double-distilled water and then ethanol, and finally allowed to air dry at room temperature [29]. This dried chip was then meticulously placed into the Q-Sense instrument. At this point, the Q-Sense instrument was primed for operation. An initial stream of double-distilled water was introduced over the electrode, serving as a background electrolyte. This preliminary step allowed for baseline measurements to be established before the introduction of the sensor's nanomaterials. To ensure the QCM signal's stability, the QCM module remained continuously supplied with double-distilled water until the QCM signal's value reached zero [30]. Following this equilibrium, a mixture comprising 2 mL of 2 ppm cobalt complex nanoparticles and 10 mL of double-distilled water was prepared. A portion of this mixture was then introduced onto the gold sensor at a controlled flow rate of 0.1 mL/min [31].

4. QCM-Monitoring of MB Dye

The QCM measurements were conducted using a dedicated QCM system (Q-sense, Biolin Scientific, Linthicum Heights, MD, USA) [32]. Each QCM measurement encompassed the introduction of 2 ppm solutions of Methylene Blue (MB) onto the surfaces of QCM-based cobalt complex nanosensors Fig [2]. This process was carried out under diverse conditions, involving varying temperatures (25°C, 35°C, and 45°C) and distinct pH values (4, 7, and 10) [33].

For each measurement, the MB solution was injected onto the surface iteratively until the signal achieved stability. This stabilization indicated the establishment of equilibrium in the binding interaction between the nanosensors and the MB molecules [34]. To eliminate unadsorbed MB from the QCM sensor surfaces, a subsequent step involved introducing double-distilled water into the QCM module. This water rinse was performed after a predetermined interval [35].

Fig. 2. depicts QCM-based sensors using cobalt complex nanoparticles for the detection of Methylene Blue (MB) in aqueous solutions.

III. RESULTS AND DISCUSSION

1. Characterization of cobalt complex nanoparticles.

Nano cobalt complex displays remarkable stability in air and is soluble in polar organic solvents, including EtOH, MeOH, DMF, and DMSO. However, it exhibits insolubility in water [36]. Elemental analysis confirms a metal-to-ligand ratio of 1:1. The cobalt complex's molar conductivity (Λm) values in DMF (10^{-3} M) at 25°C were determined to be 30 Ω^{-1} mol^{-1} cm^2, suggesting non-electrolytic behaviour [37].

Comparing the infrared spectra of the initial ligand with the corresponding cobalt complex facilitates an exploration of the coordination mechanism between the ligand and the cobalt center. The azomethine group exhibited a pronounced band at 1614 cm^{-1}, which shifted to 1604 cm^{-1} in the complexes, indicating coordination through the azomethine nitrogen atoms. The cobalt complex also displayed a distinctive band at 1678 cm^{-1} due to the presence of a CO group. Additionally, non-ligand bands were evident in the range of 416 cm^{-1} and 544 cm^{-1}, corresponding to υ(M−N) and υ(M−O) vibrations [38].

The Co(II) chelate demonstrated a multi-step decomposition pattern. The first two decomposition stages occurred within the temperature range of 30–180 °C, attributed to the loss of $_2H_2O$, with an estimated mass loss of 8.45% (calculated 8.43%). The third stage involved the release of Cl_2 gas between 180–415 °C, leading to a mass loss of approximately 16.75% (calculated 16.63%). The final three decomposition steps transpired within the 415-1000 °C range, resulting in a weight loss of about 57.23% (calculated 57.37%). This loss is associated with the organic component, leaving CoO as the residual product. The data supports the proposed formula of $[Co(L)Cl_2.H_2O].H_2O$ for the cobalt complex.

The cobalt complex exhibits distinct characteristic bands at 229 nm, 258 nm, and 370 nm in the ultraviolet region, signifying π–π* and n–π* intramolecular transitions [39].

Utilizing the disc diffusion method, cobalt complex nanoparticles were subjected to testing for their antibacterial and antifungal potential. The test encompassed a range of bacterial organisms, including Gram-positive bacteria such as Bacillus subtilis, Streptococcus faecalis, and Staphylococcus aureus, as well as Gram-negative bacteria like *Escherichia coli*, *Pseudomonas aeruginosa*, and *Neisseria gonorrhoeae*. Furthermore, fungal strains such as *Candida albicans* and *Aspergillus flavus* were also included in the assessment. The outcomes gleaned from these investigations prominently underscore the marked effectiveness of the evaluated cobalt complex nanoparticles against both Gram-positive and Gram-negative bacterial strains [40]. Additionally, the Nano Co(II) complex demonstrated potent antifungal activity, particularly notable in its effectiveness against *Aspergillus flavus.*

2. Textural characters (TEM and AFM) of cobalt complex Nano particles.

The TEM image vividly displays the dispersion pattern of the cobalt complex's synthesized particles, revealing their organization into consistent elongated structures with diameters measuring less than 100 nm Fig (4). Additionally, the surface characteristics of the synthesized nano cobalt complex underwent thorough examination using an atomic force microscope (AFM). The resulting AFM images reveal a clear fibrous morphology Fig (3.A), notably lacking any signs of aggregation or clumping. Analysis of these AFM images consistently confirms that the particle size remains below 70 nm [41].

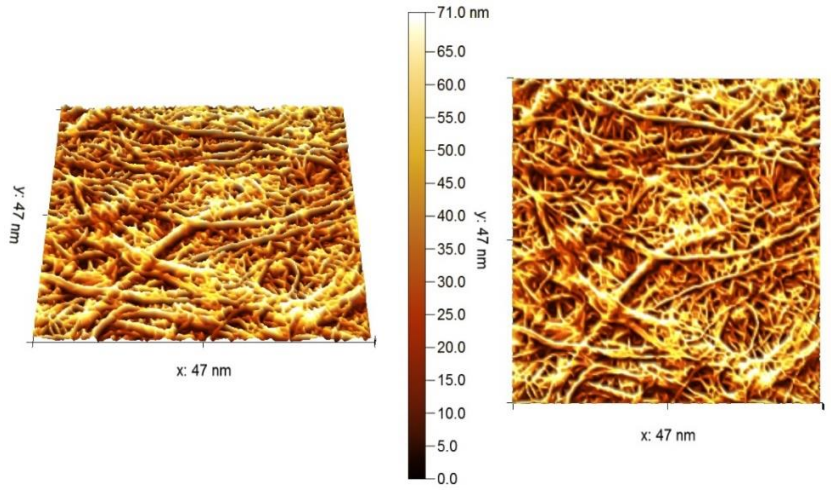

Fig (3.A) Fig(3.B)

Figure (3.A) illustrate the 3D AFM (left) and Figure (3.B) 2DAFM (right) of cobalt complex nanoparticles.

Fig.4 .The TEM image displays the dispersion pattern of the cobalt complex nanoparticles.

3. DLS and Zeta Potential

Utilizing dynamic light scattering (DLS), the particle size of the nano cobalt complex was established Fig (5).The analysis revealed an average size of 55 nm for the nano cobalt complex. The outcomes highlight a unimodal size distribution characterized by low polydispersity indices, signifying a notable level of colloidal stability within the nano cobalt complex suspension.

The Zeta potential value of -26 mV signifies a well-balanced dispersion of the nanoparticles. Zeta potential holds significance as it reflects the physicochemical stability of nanoparticles, particularly during storage conditions. A higher absolute Zeta potential value correlates with increased system stability. As demonstrated by the results, the nano cobalt complex exhibits pronounced stability [42].

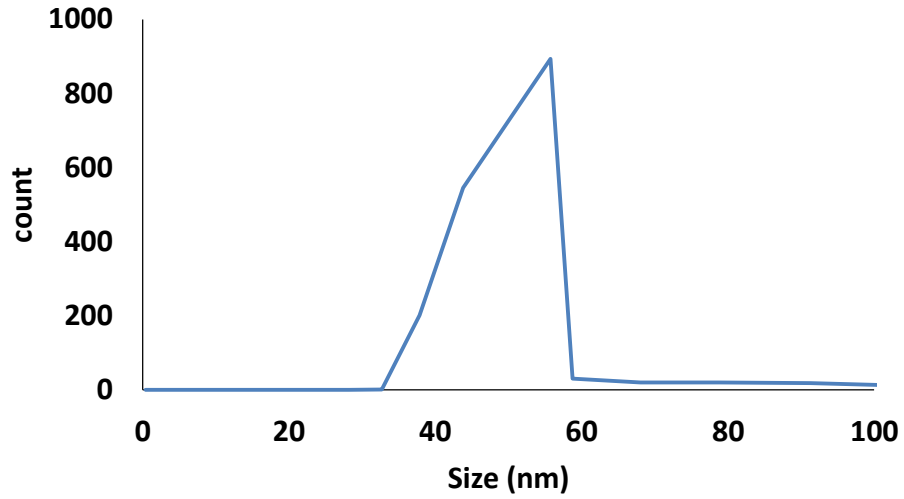

Figure. 5. illustrates the establishment of the particle size of the nano cobalt complex through dynamic light scattering (DLS).

4.BET surface area and pore size

The BET method, derived from the initials of its creators Brunauer, Emmett, and Teller, is a valuable technique for characterizing nanoscale materials. It relies on the physical adsorption of gases onto solid surfaces. This method is frequently employed to determine the surface area of nanostructures due to its effectiveness, speed, and simplicity [43]. The utilization of BET adsorption isotherms facilitated the evaluation of surface area characteristics of the nano cobalt complex sample Fig. 6.

According to De Boer's classification, hysteresis loop isotherm curves are categorized into four types to discern the nature of porosity. The observation that each sample of cobalt complex nanoparticles displays type IV nitrogen adsorption-desorption isotherms with a hysteresis loop confirms their macroporous nature. The multipoint BET surface area measures 74.1 m^2/g, with a DH pore volume of 58.1 cc/nm. This substantial multipoint BET surface area not only enhances the nanoparticles' capacity for adsorbing MB in aqueous solutions but is also likely influenced by the fibrous morphology of the metal complex nanoparticles. Notably, the presence of macropores amplifies the adsorption of MB onto the surface of the metal complex nanoparticles.

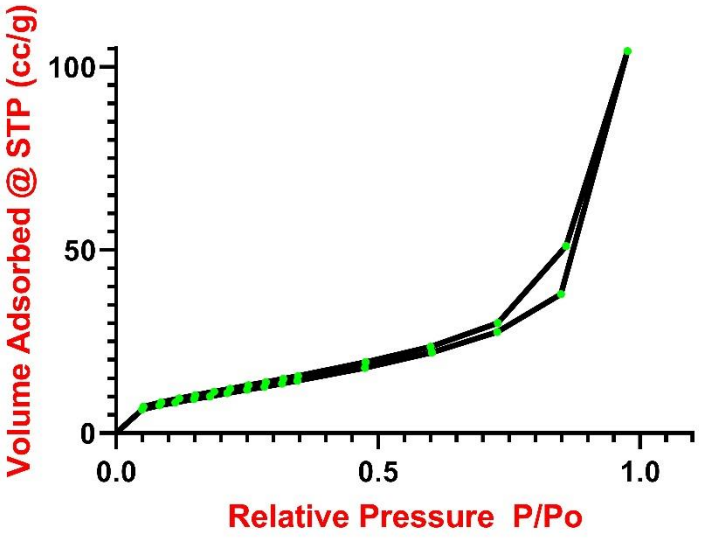

Fig. 6. N_2 adsorption-desorption isotherm of the surface area characteristics of the nano cobalt complex sample.

5. Contact angle, Hydrophobicity and toxicity of cobalt nano complex

The water contact angle measurement indicated that the nano cobalt complex particles exhibit hydrophobic properties, displaying an angle of 121°. This hydrophobic nature significantly augments the potential of these nanoparticles to serve as effective water sensors.

When developing environmentally friendly nano particle-based sensors, it's imperative to employ materials that are non-toxic. To ensure this, the cytotoxicity of the nano cobalt complex was thoroughly assessed, revealing an IC50 value of 220 µg/ml. This substantial IC50 value reinforces the viability of utilizing the nano cobalt complex as a water sensor, underscoring its potential safety and applicability in such applications.

6. MB Monitoring Using QCM-Based Nano cobalt sensors

In the typical experiments involving a QCM-based nano cobalt complex sensor, the process unfolds through four distinct stages:

1. Baseline Response: at this stage, the initial frequency response of the nanosensors establishes a stable baseline.

2. Sudden Frequency Drop: an abrupt decrease in frequency occurs due to the rapid binding of methylene blue (MB) molecules to the sensors. This effect is attributed to the abundance of vacant sites on the sensors' surfaces.

3. Enhanced MB Adsorption: the subsequent stage involves the heightened adsorption of the target MB molecules onto the sensor surfaces.

4. Equilibrium State: the fourth stage signifies the attainment of an equilibrium state in the adsorption process between the nano cobalt complex and MB molecules.

During the introduction of the nano cobalt complex, the frequency shift remains steady before the MB solution enters the QCM system. However, when MB is absorbed onto the surface of the QCM-based cobalt complex nanosensors, a significant change in frequency occurs. As indicated in the figure, this suggests the QCM-based Cobalt complex nanosensor effectively binds with MB molecules, generating a noticeable response to the adsorption process.

Following this, as the frequency stabilizes once more, it signifies the achievement of an equilibrium state in MB adsorption on the surface of the QCM-based nano cobalt complex sensor. During the fourth step, no discernible alterations in sensor frequency are observed, indicating minimal mass loss and minor structural modifications on the nanosensor surfaces. This underscores the potential utility of the QCM nano cobalt complex sensor for real-time detection of MB dye.

Proposed Sensing Mechanism of the QCM-Based nano cobalt complex

Given that the N atom within MB possesses lower electronegativity in contrast to oxygen atom presented in the nano cobalt complex sensor, a scenario emerges where the O atom bears a partial negative charge while the N atom assumes a partial positive charge. Consequently, this gives rise to the potential for dipole-dipole interactions, primarily originating from π–π interactions. Furthermore, the inclusion of polar side chains in the nano cobalt complex, acting as functional groups with electron donors, intensifies the negative charge density. This enhanced charge distribution amplifies the propensity of the QCM-based nano cobalt sensor to engage in interactions with MB. This interaction is facilitated not only through electrostatic forces but also through π–π interactions.

7. Effect of temperature on sensor performance

Temperature significantly influences chemical reactions; thus, a specific reaction can be enhanced or hindered depending on the conditions of the reactants and products. This influence is particularly noteworthy due to the interplay between the surroundings and the reaction itself. A temperature alteration leads to accelerated diffusion of the adsorbate molecule through the exterior boundary layer and the internal pores of the adsorbent. Furthermore, modifying the temperature amplifies the adsorbent's capability to attain equilibrium concerning a given adsorbate.

To assess the impact of temperature on MB monitoring, experiments were conducted at 25°C, 35°C, and 45°C, employing the nano cobalt complex sensor. The results, as depicted in the figure, unveiled that the detection sensitivity of MB in aqueous solutions is intricately influenced by the temperature of the medium Fig.7.

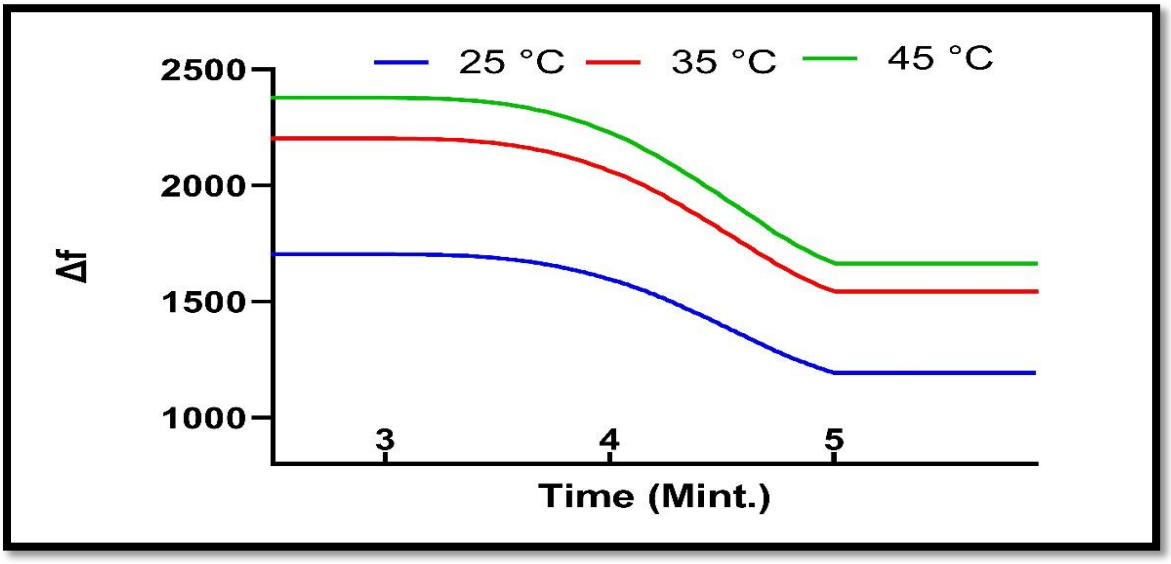

Fig .7. Thermal Influence on Adsorption Dynamics: Exploring Temperature's Impact on Methylene Blue Monitoring Using Nano Cobalt Complex Sensor

It was observed that with increasing temperature from 25°C to 45°C, an unusual rise in frequency shifts occurred, contrary to the behavior seen in the QCM-based nano cobalt sensor, where the frequency shifts displayed an ascending pattern. This phenomenon can be attributed to the interaction mechanism between the QCM-based nano cobalt sensor and cationic MB molecules, which hinges on the electrostatic attraction between the highly negatively charged sensor surface and the positively charged MB molecules.

The increase in temperature might lead to greater diffusion of MB molecules within the solution. As a result, the attachment of MB dye to the surface of the QCM-based nano cobalt sensor could be compromised. Furthermore, at higher temperatures, the breaking of bonds within the reactive groups on the surface of the QCM-based nano cobalt sensor could reduce the number of active adsorption sites. This decrease in available sites could contribute to a reduction in the amplitude of MB's adsorption.

Remarkably, the adsorption of MB onto the surface of the QCM-based nano cobalt sensor triggers a noticeable alteration in frequency due to the mass of MB molecules adsorbed onto the sensor surfaces.

8. Effect of different pH on sensor performance

Dye adsorption experiences substantial variations influenced by the pH of the solution. When dyes are introduced into water, they disassociate and ionize, generating electrostatic charges within the solution [44, 45]. The nature and quantity of these electrostatic charges depend on the pH of the solution. Consequently, within an adsorption system, the attraction and adherence of a specific dye to the adsorbent will fluctuate with pH. This variation arises due to the principle that opposite electrostatic charges draw together, while identical charges repel. Thus, the highest adsorption of MB occurs when the solution is at its most acidic pH level.

In the context of methylene blue (MB), an alkaline or high-pH solution triggers a reaction that leads to the degradation of MB^+ a cationic thiazine dye and the emergence of methylene violet blue Fig [8, 9]. This shift can be attributed to the reduction of positive charges on methylene blue molecules. Consequently, the electrostatic attraction between MB and the negatively charged nano cobalt sensor weakens. This weakening interaction results in an increase in frequency, as depicted in the Fig.10.

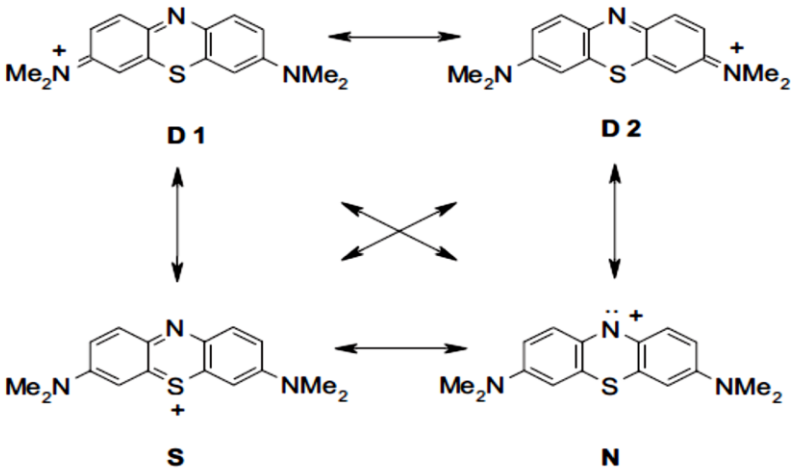

Fig. 8. Major valence bond resonance structures of MB. Alternative Kekule structures of benzenoid rings and charged-carbon mesomers are not shown [45].

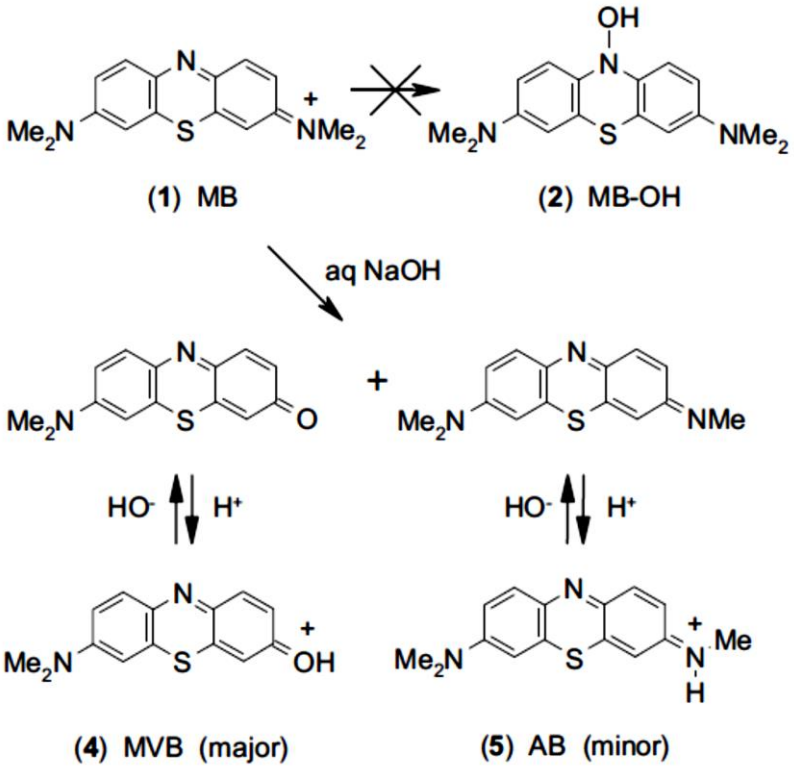

Fig. 9. Summary of reactions of MB at different pH.

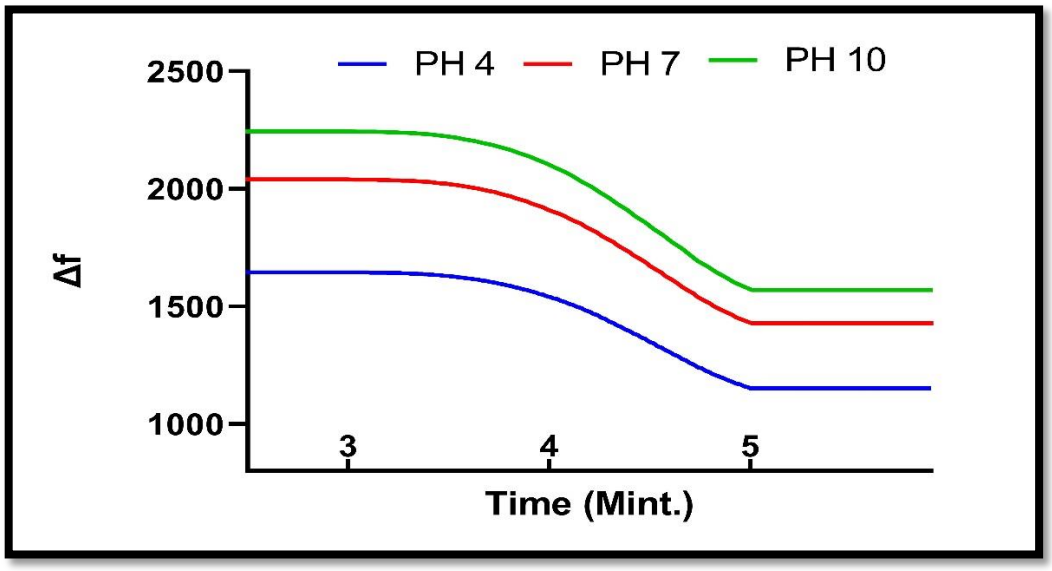

Fig. 10. Effect of different pH on the performance of nano cobalt complex QCM sensor

V –CONCLUION

In this work, novel nano cobalt sensor have been developed for comparable detection of MB in the water streams. The DLS and Zeta values revealed that the nano cobalt sensor possess a particles size distribution of 55 nm, and zeta potentials of -26mV. While the TEM and AFM images depicted that the have a homogenous fiber or rod.

Subsequently, the fabricated nanomaterials were employed as novel nanosensors based on the QCM method. The designed nanosensors were further used to monitor the low concentrated MB of about 1 ppm at different temperatures (25 C, 35 C, and 45 C) and different pH (4, 7, 10) .Accordingly, it could be stated that the QCM-based cobalt cpomplex nanoparticle is an efficient tool as a real-time rapid (reponse time 3 minutes) and sensitive nanosensor for MB detection in continuous-flow water streams.

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