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ARTICLE

Development of an Electrochemical Sensor for the Treatment of Scaling in the Presence of *Herniaria hirsuta*

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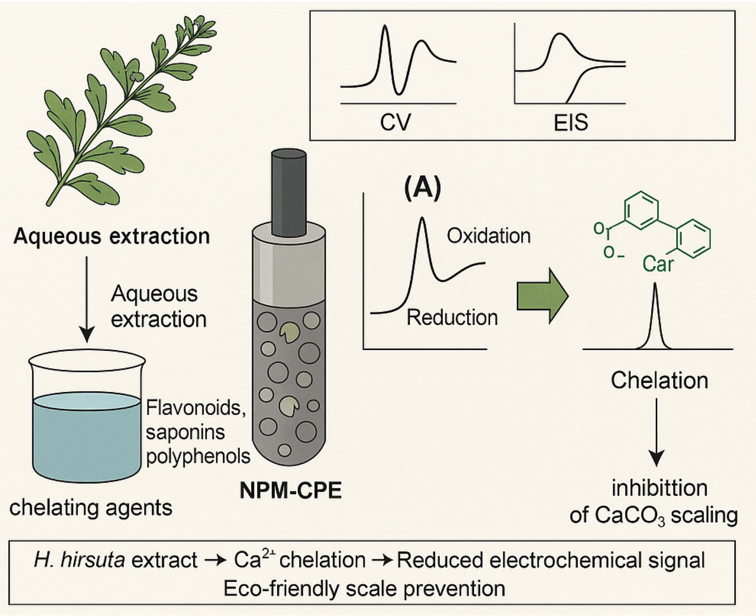

The formation of calcium carbonate ($CaCO_3$) scale presents a significant challenge in various industrial systems, impairing efficiency and increasing maintenance costs. In pursuit of environmentally friendly solutions, this study investigates the chelating potential of *Herniaria hirsuta* extract, a plant known for its rich phytochemical profile against Ca^{2+} ions, using an electrochemical approach. A natural phosphate-modified carbon paste electrode (NPM-CPE) was developed and characterized via cyclic voltammetry (CV), square wave voltammetry (SWV), and electrochemical impedance spectroscopy (EIS). The NPM-CPE sensor demonstrated enhanced electrochemical performance and clear detection of Ca^{2+} ions through defined redox peaks. Upon introduction of the *Herniaria hirsuta* extract, these signals were significantly attenuated, indicating effective complexation and chelation of calcium ions. The EIS results further confirmed this interaction by showing increased electron transfer resistance in the presence of the plant extract. These findings highlight the potential of *Herniaria hirsuta* as a green, cost-effective agent for scale prevention and underscore the synergy between natural resources and electrochemical sensing technologies for sustainable industrial applications.

Keywords: *Herniaria hirsuta*, Ca^{2+} chelation, scale inhibition, electrochemical sensor, NPM-CPE, voltammetry, EIS, green chemistry

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INTRODUCTION

The formation of mineral deposits, particularly calcium carbonate ($CaCO_3$), represents a major problem in many industrial systems such as cooling circuits, boilers, and heat exchangers. This phenomenon, known as scaling, leads to reduced energy efficiency, increased maintenance costs, and a significant environmental impact.[1–3] In response to these challenges, industries are increasingly turning toward sustainable and eco-friendly solutions capable of preventing the precipitation and accumulation of mineral salts.

Within this context, the use of natural materials and environmentally benign processes aligns with the principles of green chemistry. Medicinal plants, rich in bioactive compounds, offer great potential for developing low-cost, biodegradable scale inhibitors. Among these, *Herniaria hirsuta* L. traditionally used in North African medicine for the treatment of kidney stones, has attracted particular attention due to its abundance of polyphenols, flavonoids, and saponins, which are known for their strong metal-ion chelating abilities.[4–8]

Several studies have demonstrated the effectiveness of *Herniaria hirsuta* in preventing or reducing calcium oxalate crystallization, thus confirming its complexing activity toward calcium ions.[4–7] Meanwhile, recent works have employed voltammetry and electrochemical impedance spectroscopy to investigate metal–ligand interactions or to develop electrochemical sensors sensitive to various metal cations.[9–15]

The use of modified electrodes especially carbon paste electrodes doped with natural materials such as natural phosphate has shown significant improvements in conductivity, active surface area, and selectivity toward metal ions.[11,21]

These approaches have enhanced understanding of adsorption and complexation phenomena; however, they have mainly focused on analytical detection or metal corrosion, without integrating natural materials with an environmental purpose for scale prevention.

Despite these advances, several limitations remain. Most studies on *Herniaria hirsuta* have concentrated on its biomedical applications (kidney stone prevention) rather than its potential industrial use as a green antiscaling agent. Few investigations have attempted to couple the plant's chelating properties with electrochemical platforms to monitor, in real time, interactions between Ca^{2+} ions and bioactive compounds. Furthermore, existing studies on modified electrodes have not explored the incorporation of natural phosphate, a local, inexpensive, and eco-friendly mineral resource into the conductive matrix to enhance sensor sensitivity and durability.

Thus, the synergistic combination of *Herniaria hirsuta* and a natural phosphate–based electrochemical sensor remains unexplored, although it could provide an innovative and sustainable pathway for calcium scale prevention.

The present study aims to develop and characterize an electrochemical sensor based on a natural phosphate–modified carbon paste electrode (NPM-CPE) to evaluate, through voltammetry and electrochemical impedance spectroscopy, the complexation behavior of Ca^{2+} ions in the presence of an aqueous extract of *Herniaria hirsuta*.

The main objective is to demonstrate the plant's ability to trap calcium ions, thereby validating its potential as a natural antiscaling agent. This work introduces a dual innovation: the integration of a local mineral material (natural phosphate) to enhance electrochemical performance, and the use of a multifunctional plant extract for eco-friendly scale control.

Hence, this study proposes an original approach combining natural resources and advanced electrochemical technologies to develop green and economically viable solutions for industrial scale prevention.

Herniaria hirsuta

Herniaria hirsuta L., commonly known as Hairy Rupturewort in English, is referred to as Hashishat Al-Fatik, Marda, Noman Amrad, or Dizama in Arabic-speaking regions. It is also recognized by various vernacular names such as Herniaire velue (French), Behaartes Bruchkraut (German), and Luddknytling (Swedish).[16]

This species exhibits a broad geographical distribution, extending across multiple continents. In Africa, it is found in countries such as Morocco, Algeria, Egypt, and Ethiopia. In Asia, it is present in the Middle East and Central Asia, including Iran, Iraq, Syria, Lebanon, Jordan, Palestine, Turkey, Armenia, Azerbaijan, the Russian Federation, Kuwait, and the Central Asian republics of Kyrgyzstan, Tajikistan, Turkmenistan, and Uzbekistan. Its range also spans large portions of Europe, with recorded occurrences in Austria, Belgium, Germany, Switzerland, Hungary, Slovakia, Albania, Bulgaria, Croatia, Greece, Italy, North Macedonia, Romania, Slovenia, France, Spain, and Portugal.[17] Such widespread distribution underscores the ecological adaptability and ethnobotanical significance of *Herniaria hirsuta* across diverse climatic and cultural regions (Figure 1).

Figure 1. *Herniaria hirsuta*.

Chemical constituents

Phytochemical profiling of *Herniaria hirsuta* reveals a remarkable abundance of bioactive secondary metabolites, notably phenolic compounds, flavonoids, flavonols, and saponins. Quantitative analyses indicate that the plant possesses a total flavonoid content of approximately 4.51%, while the saponin content reaches 12.74%.[18] In lyophilized aqueous infusions, high concentrations of specific phytoconstituents were recorded, including phenolics (90 ± 1 mg GAE[a]/g), flavonoids (46 ± 3 mg CE[a]/g), esters (38 ± 1 mg CAE[a]/g), and flavonols (26 ± 1 mg QE[a]/g).[19] Moreover, both ethanolic and aqueous extracts of *H. hirsuta* exhibit substantial levels of these compounds. The ethanolic extract contained 28.2 mg GAE/g of phenolics, 4.6 mg CE/g of flavonoids, 12.1 mg GAE/g of tannins, 3.4 mg C_3GE[a]/g of anthocyanins, and 16.2 mg QSE[a]/g of saponins. The corresponding aqueous extract displayed slightly lower but still significant concentrations: 22.4 mg GAE/g (phenolics), 3.7 mg CE/g (flavonoids), 8.2 mg GAE/g (tannins), 3.8 mg C_3GE/g (anthocyanins), and 8.4 mg QSE[a]/g (saponins).[20] These findings confirm the rich phytochemical composition of *Herniaria hirsuta*, highlighting its potential for diverse pharmacological and environmental applications.

MATERIALS AND METHODS

Electrochemical measurement

This section presents an in-depth analysis of the electrochemical investigations performed to elucidate the complexation behavior of *Herniaria hirsuta* extract toward Ca^{2+} ions, employing natural phosphate-modified carbon paste electrodes (NPM-CPE) as sensitive electrochemical sensors.

Reagents and chemicals

All reagents used in this investigation were of analytical grade and employed without further purification. Spectroscopic-grade graphite powder (RWB, Rings Dorff-Werke GmbH, Bonn-Bad Godesberg, Germany) was procured from Aldrich. Calcium nitrate ($Ca(NO_3)_2$) was supplied by Merck Chemicals. Deionized water

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[a] GAE: gallic acid equivalents; CE: catechin equivalents; CAE: citric acid equivalents; QE: quercetin equivalents; C_3GE: cyanidin-3-glucoside equivalents; QSE: Quillaja saponin equivalents.

was consistently used for the preparation of all solutions to ensure the highest purity standards. Additionally, a plant-based extract derived from *Herniaria hirsuta* was incorporated as a functional component in the experimental protocol.

Electrochemical apparatus

Electrochemical investigations were carried out using a Voltalab PGSTAT 100 potentiostat (Eco Chemie B.V., Utrecht, Netherlands), operated via the Voltalab Master 4 software suite for data acquisition and analysis. All measurements were performed in a conventional single-compartment electrochemical cell configured with a three-electrode system. The saturated calomel electrode (SCE) was employed as the reference electrode, while a platinum wire functioned as the counter electrode. All reported potentials are referenced against the SCE. The working electrode consisted of a carbon paste electrode (CPE) modified with the appropriate active material, tailored for enhanced electrochemical performance.

Electrode preparation

The fabrication of the carbon paste electrode (CPE) involved the thorough homogenization of graphite powder with paraffin oil to obtain a conductive and malleable matrix. For the preparation of the natural phosphate-modified carbon paste electrode (NPM-CPE), an equivalent proportion of graphite was systematically replaced by finely ground natural phosphate. Subsequently, paraffin oil was incorporated to achieve the desired paste consistency. The composite was meticulously blended using a mortar and pestle to ensure uniform dispersion of the components. The resulting paste was then tightly packed into the electrode cavity, and its surface was carefully polished to obtain a smooth and reproducible working interface.[21]

Electrochemical measurement and characterization

In order to investigate the electrochemical performance of the modified electrodes and elucidate the complexation capability of *Herniaria hirsuta* extract toward Ca^{2+} ions, a comprehensive suite of electrochemical techniques was employed, including cyclic voltammetry (CV), square wave voltammetry (SWV), and electrochemical impedance spectroscopy (EIS). These methods provided valuable insights into the interfacial charge transfer processes, enabling a detailed analysis of the redox behavior and the coordination interactions between Ca^{2+} ions, the phytochemical constituents of the *H. hirsuta* extract, and the surface of the functionalized electrodes.

Extraction of Herniaria hirsuta

The extraction of bioactive constituents from *Herniaria hirsuta* leaves was carried out using a solid–liquid extraction technique. Precisely 50 g of finely ground leaf material was introduced into an Erlenmeyer flask, followed by the addition of 500 mL of solvent, maintaining a 1:10 (w/v) ratio to ensure efficient mass transfer. The flask was hermetically sealed with aluminum foil to minimize solvent evaporation and protect light-sensitive compounds. Two extraction methods were employed: maceration at ambient temperature with continuous magnetic stirring for 24 hours, or reflux-assisted extraction at 60–70 °C for 2–3 hours to enhance compound solubilization. Upon completion, the extract was subjected to vacuum or gravity filtration through Whatman filter paper to separate the liquid phase from the plant residue. To ensure maximal yield, the remaining solid matrix was washed with a small volume of fresh solvent. The combined filtrates were subsequently concentrated under reduced pressure using a rotary evaporator at low temperature, thus preserving thermolabile phytochemicals. The resulting concentrated extract was collected in a sterile, amber glass container and stored at low temperature in the absence of light to maintain its chemical stability and bioactivity (see Figure 2).

Figure 2. Schematic illustration of the extraction process of the *Herniaria hirsuta* plant.

RESULTS AND DISCUSSION

Cyclic voltammetry and square wave voltammetry experiments

Figure 3 shows a cyclic voltammogram (CV) recorded in a KCl solution using carbon paste electrodes (CPE) and natural phosphate-modified carbon paste electrodes (NPM-CPE) at a scan rate (SR) of 50 mV/s. The comparison of the CVs for the two types of electrodes (CPE and NPM-CPE) allows us to observe the differences in their electrochemical behavior. Typically, NPM-CPE electrodes are expected to demonstrate superior electrochemical performance due to their larger active surface area and enhanced conductivity compared to traditional CPE electrodes.

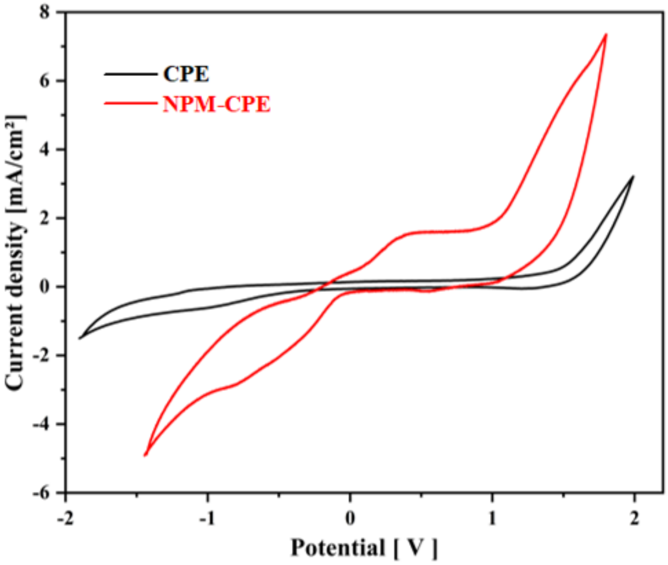

Figure 3. CV recorded in a KCl solution, at CPE and NPM-CPE, with a SR of 50 mV/s.

The positions and intensities of the oxidation and reduction peaks in the voltammograms can provide information about the electron transfer processes occurring at the electrode surface. Sharper and more defined peaks in the case of NPM-CPE would show better reaction kinetics. The analysis of peak currents (the maximum current values during oxidation and reduction) can give an indication of the electrode's ability to catalyze redox reactions. An NPM-CPE electrode would generally show higher peak currents due to its larger active surface area and greater catalytic efficiency. The shape of the curves in the CV can also provide insights into the reaction mechanisms and diffusion phenomena occurring at the electrode surface. A more symmetrical shape and closer peak separation in the case of NPM-CPE may mention faster reaction kinetics and better electrochemical reversibility. These results are confirmed by square wave voltammetry in Figure 4.

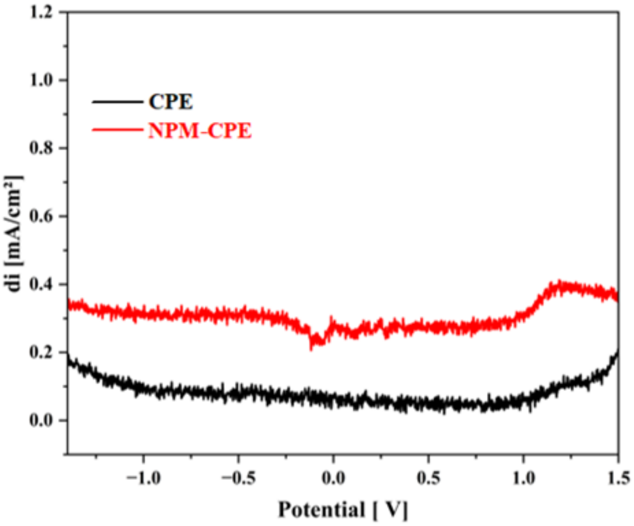

Figure 4. SWV recorded in a KCl solution, at CPE and NPM-CPE, with a SR of 50 mV/s.

Electrochemical response of the CPE electrode to Ca^{2+} ions

The cyclic voltammogram (CV) obtained at the surface of the unmodified carbon paste electrode (CPE) in an electrolyte medium containing Ca^{2+} ions (Figure 5) exhibits a characteristic passive electrochemical behavior toward calcium species. This is evidenced by the absence of any discernible redox peaks within the potential window explored, indicating that under the experimental conditions employed, calcium ions do not undergo electron transfer reactions at the bare CPE surface. The lack of electroactivity represent either the high thermodynamic stability of Ca^{2+} ions in solution, a sluggish electron transfer kinetics, or an insufficient affinity of the unmodified electrode surface for calcium ion complexation or adsorption. This passive response underlines the necessity of electrode surface modification to facilitate any possible electrocatalytic or sensing activity toward Ca^{2+} detection.

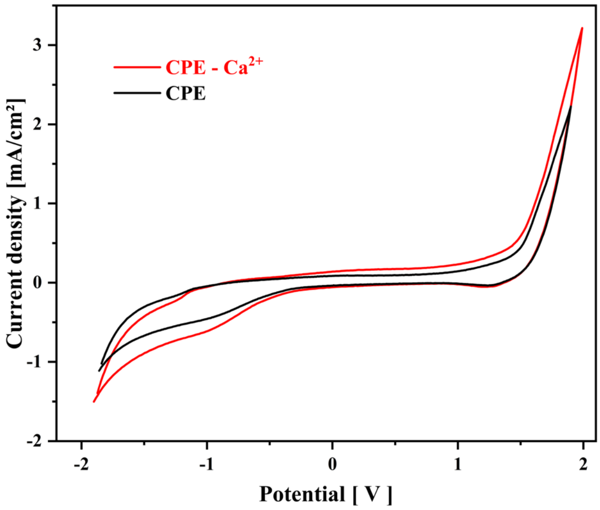

Figure 5. CV recorded in KCl, with and without Ca^{2+} ions, at CPE, at a scan rate of 50 mV/s.

Electrochemical response of the NPM-CPE electrode to Ca^{2+} ions

The electrochemical signature of Ca^{2+} ions in the electrolytic medium is clearly evidenced in the cyclic voltammogram (CV) recorded for the NPM-CPE electrode (Figure 6). Two well-defined redox processes are observed, highlighting the active participation of calcium species in the interfacial electrochemical phenomena.

The first redox feature appears at approximately -0.2 V during the cathodic scan, near the end of the potential window. This peak can be attributed to the reduction of Ca^{2+} ions to metallic calcium. The well-resolved nature of this cathodic signal as a result a relatively facile and localized electron transfer process involving Ca^{2+} at the electrode–electrolyte interface.

Upon reversing the scan direction, a broad anodic peak is recorded around 1.2 V. This anodic process corresponds to the oxidation of metallic calcium previously deposited during the cathodic scan. The breadth of this oxidation peak may reflect a distribution of calcium species in different chemical or physical environments, likely due to their partial entrapment within the natural phosphate matrix. The heterogeneous nature of the oxidation process is indicative of a complex solid-state dissolution mechanism rather than a simple surface-limited redox reaction.

Taken together, the presence of these two redox peaks strongly supports the reversible intercalation and deintercalation behavior of Ca^{2+} ions within the natural phosphate-modified carbon paste electrode (NPM-CPE), affirming the electrode's potential for calcium-ion electrochemistry applications.

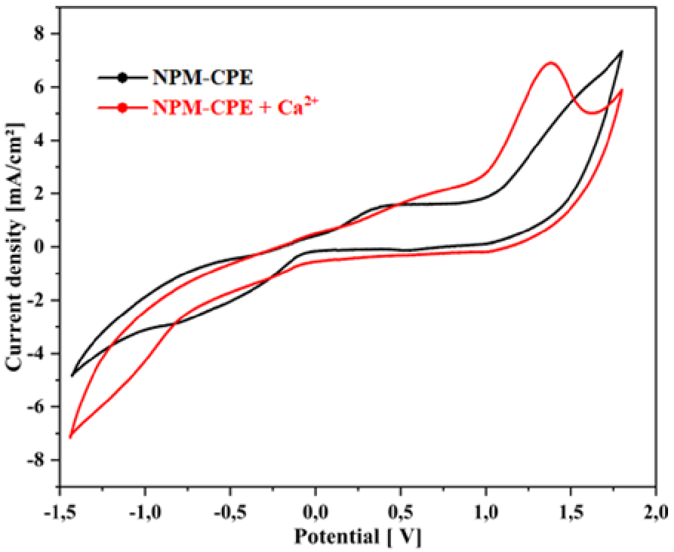

Figure 6. CV recorded in KCl, with and without Ca^{2+} ions, at NPM-CPE, at a scan rate of 50 mV/s.

Complexation effect of Herniaria hirsuta plant extract on Ca^{2+} ions

In this experiment, the extract of the plant *Herniaria hirsuta* was introduced into the KCl medium containing Ca^{2+} ions, and subsequently, CVs were recorded on the NPM-CPE surface. Notably, the addition of the *Herniaria hirsuta* plant extract to KCl with Ca^{2+} ions led to the disappearance of redox peaks in the CV. This observation strongly advises that the *Herniaria hirsuta* plant extract effectively chelated the Ca^{2+} ions.

Figure 7 represents the CV of the modified electrode with Ca^{2+} ions under similar conditions. The apparent differences in the shapes of these CVs may be due to variations in experimental conditions or specific characteristics of the studied systems. The differences observed express the possibility of strong complexation of Ca^{2+} ions upon the addition of the *Herniaria hirsuta* plant extract, although the oxidation potential mentioned in Figure 8 was around 1.2 V.

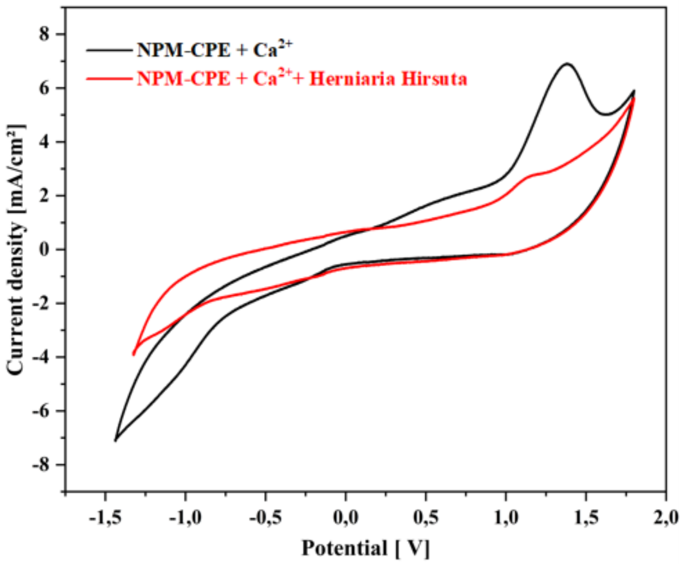

Figure 7. CV was recorded in KCl solutions, in the presence of Ca^{2+}, with and without *Herniaria hirsuta*, at a scan rate of 50 mV/s.

The square wave voltammetry (SWV) highlighted the influence of *Herniaria hirsuta* on Ca^{2+} ions, revealing a well-defined redox signal (Figure 8) that almost disappeared after the introduction of the plant extract. The attenuation of the peak around 1.2 V on the cyclic voltammetry (CV) curve in the presence of *Herniaria hirsuta* represents a significant finding. This alteration may be related to specific electrochemical interactions induced by the plant, suggesting the need for further studies to better understand the underlying mechanisms.

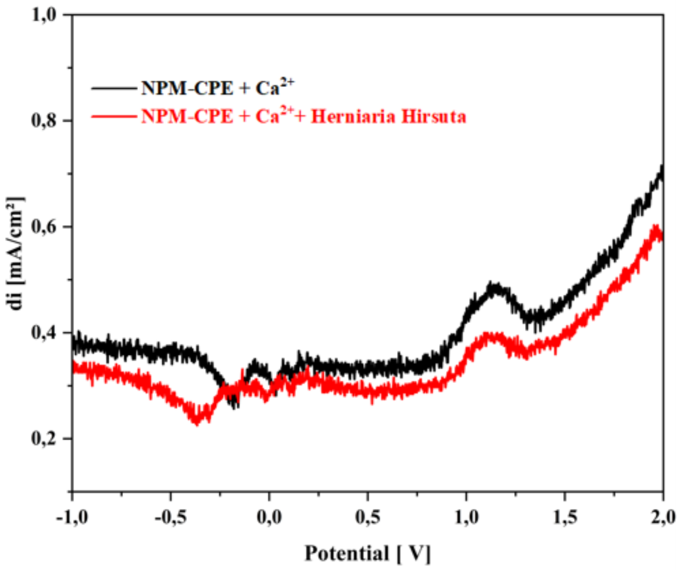

Figure 8. SWV was recorded in KCl solutions, in the presence of Ca^{2+}, with and without *Herniaria hirsuta*, at a scan rate of 50 mV/s.

Electrochemical Impedance Spectroscopy (EIS) analysis provided deeper insight into the chelation mechanism of Ca^{2+} ions by the *Herniaria hirsuta* extract (Figure 9). The Nyquist plots revealed a significant increase in the semicircle diameter upon the addition of the plant extract to the Ca^{2+} containing solution. This increase corresponds to a substantial elevation in the charge transfer resistance (Rct), which is a direct electrochemical manifestation of hindered ionic mobility and interfacial electron exchange processes at the electrode surface.

The observed augmentation in Rct can be rigorously interpreted as a consequence of the complexation of Ca^{2+} ions by the bioactive phytochemicals present in the *Herniaria hirsuta* extract likely including flavonoids, saponins, tannins, and other polyphenolic compounds with known metal-chelating properties. The reduction in free, electrochemically active Ca^{2+} species in the bulk solution results in a diminished availability of these cations to participate in interfacial charge transfer reactions, thereby elevating the impedance response.

This chelation phenomenon aligns with the thermodynamic principles governing complex formation, where the stability constants of metal-ligand interactions favor the formation of stable organometallic complexes in solution. The EIS findings thus provide compelling electrochemical evidence supporting the sequestration of Ca^{2+} ions by the phytoconstituents of *Herniaria hirsuta,* reinforcing the extract's potential utility in modulating calcium-mediated processes, including but not limited to, the inhibition of calcium salt crystallization in biological or physicochemical systems.

In summary, the substantial increase in the semicircular domain of the Nyquist spectrum serves as a diagnostic electrochemical fingerprint for the efficient binding and immobilization of Ca^{2+} ions, corroborating the extract's role as a potent natural complexing agent.

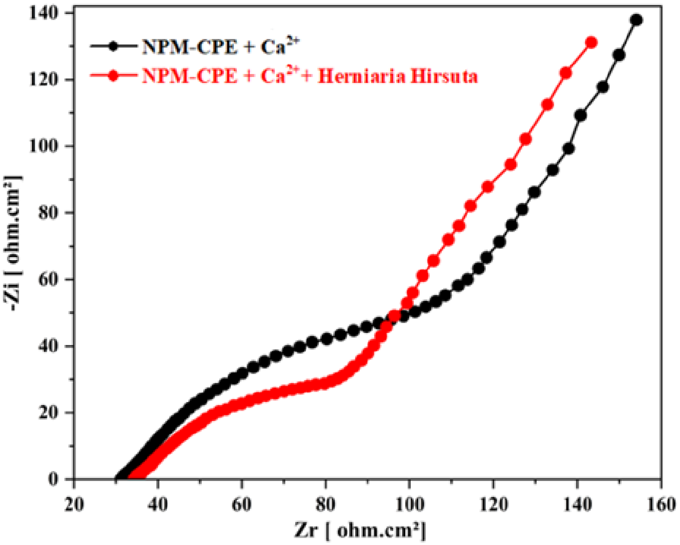

Figure 9. EIS was recorded in KCl solutions, in the presence of Ca^{2+}, with and without *Herniaria hirsuta*, at a scan rate of 50 mV/s.

Figure 10 shows the cyclic voltammetry (CV) curves obtained for the carbon paste electrode (CPE) in the presence of Ca^{2+} ions, with varying concentrations of the aqueous extract of *Herniaria hirsuta* leaves. As the concentration of the *Herniaria hirsuta* extract increases, the oxidation and reduction peaks of Ca^{2+} progressively decrease. At higher concentrations, the reduction peak of Ca^{2+} completely disappears.

This behavior is likely due to the high polyphenol content of the *Herniaria hirsuta* extract. Polyphenols are well-known for their strong metal-chelating properties.[22-24] In particular, deprotonated phenolic groups exhibit high charge density, making them hard ligands capable of effectively binding Ca^{2+} ions.

The proposed electrochemical mechanism can be described in three steps:

Accumulation (Ca^{2+}) solution + NPM-CPE → (Ca^{2+} / NPM-CPE) adsorption (1)

Reduction (Ca^{2+}/ NPM-CPE) adsorption + 2e^{-} → (Ca / NPM-CPE) adsorption (2)

Anodic redissolution (Ca / NPM-CPE) adsorption →(Ca^{2+}) solution + (NPM-CPE) surface + 2e^{-} (3)

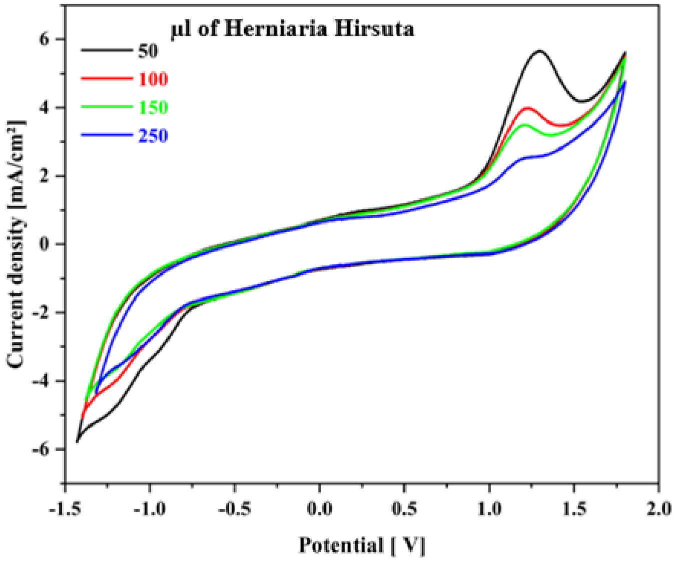

Figure 10. CV were recorded at the NPM-CPE electrode in a 1 M KCl solution containing *Herniaria hirsuta* extract, at a scan rate of 50 mV/s, effect of *Herniaria hirsuta* concentrations.

Figure 11 presents the electrochemical impedance spectroscopy (EIS) spectra recorded for various increasing concentrations of *Herniaria hirsuta* extract, designated as V_1 to V_4. A detailed analysis of these spectra reveals a progressive increase in the diameter of the capacitive semicircle as the extract concentration increases.

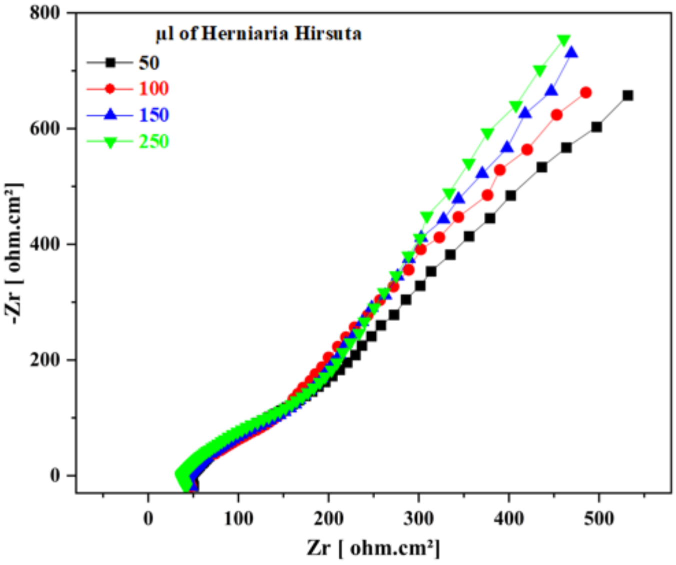

Figure 11. EIS were recorded at the NPM-CPE electrode in a 1 M KCl solution containing *Herniaria hirsuta* extract, at a scan rate of 50 mV/s, effect of *Herniaria hirsuta* concentrations.

This trend highlights a significant rise in the charge transfer resistance (R_{ct}), which is generally interpreted as an improvement in the passivation of the metal surface. This behavior offer that the bioactive compounds present in the extract interact more strongly with the electrode surface at higher concentrations, forming either a more compact protective layer or more stable surface complexes. This enhanced electrochemical response thus reflects increased inhibitory efficiency, attributable to a more pronounced adsorption of the active constituents onto the metal surface, in accordance with the Langmuir model or a pseudo-linear chemisorptive adsorption behavior.

Table I provides a comprehensive summary of the electrochemical parameters derived from the electrochemical impedance spectroscopy (EIS) data. A pronounced and systematic increase in the double-layer capacitance (C_{dl}) is observed with the progressive addition of *Herniaria hirsuta* extract, indicating enhanced interfacial activity at the metal/solution interface. This trend strongly supports the hypothesis of effective adsorption of phytochemical constituents from the extract onto the metallic surface. From a physicochemical standpoint, the observed rise in Cdl reflects a substantial alteration of the interfacial structure, likely due to the formation of a more compact, homogenous, and dielectric-rich adsorption layer. The increased dielectric constant and the reduced effective thickness of the electrical double layer, as described by the Helmholtz model, point to the accumulation of organic molecules at the interface, thereby increasing the surface coverage and modifying the interfacial capacitance. This behavior is in strong agreement with the results previously obtained from polarization curves and weight loss measurements, both of which demonstrated improved corrosion inhibition efficiency with increasing extract concentration. Mechanistically, the enhancement in Cdl serves as an indirect yet reliable indicator of the adsorption of active inhibitor molecules, proposing their ability to form coordination bonds or π–d interactions with the metal surface. This leads to the development of a protective barrier that impedes charge transfer processes, thus mitigating corrosion reactions. Collectively, these electrochemical findings substantiate the effectiveness of *Herniaria hirsuta* extract as a potent green corrosion inhibitor and reinforce the conclusions drawn from complementary experimental techniques.

Table I. Electrochemical parameters from EIS

Drops	Diameters (Ohm.cm^2)	Correlation	R_1 (Ohm.cm^2)	R_2 (Ohm.cm^2)	R_2 - R_1 (Ohm.cm^2)	C (µF/cm^2)
1	368.4	0.957	50.01	337	286.99	336.2
2	626.3	0.992	43.64	530.2	486.56	213.7
3	642.9	0.997	42.54	551.5	508.96	205.4
4	666	0.998	36.73	574.1	537.37	197.3

CONCLUSION

This study rigorously demonstrates the effectiveness of an electrochemical sensor based on carbon paste modified with natural phosphate (NPM-CPE) for the detection of calcium ions (Ca^{2+}) in aqueous media. The sensor was developed through the synergistic integration of low-cost, naturally derived materials with advanced electroanalytical techniques, aiming to achieve high sensitivity and selectivity toward divalent cations.

Electrochemical characterization using cyclic voltammetry (CV), square wave voltammetry (SWV), and electrochemical impedance spectroscopy (EIS) revealed distinct redox peaks corresponding to the presence of Ca^{2+} ions. These responses demonstrate a strong electrochemical affinity of the NPM-CPE sensor for calcium ions, as well as efficient electron transfer kinetics at the electrode–solution interface key indicators of the sensor's analytical performance.

The addition of an aqueous extract of *Herniaria hirsuta*, a plant known for its anti-lithiasis properties, led to a marked decrease or disappearance of electrochemical signals from free Ca^{2+}, indicating chelation by phytochemicals such as flavonoids or saponins. This was further supported by EIS measurements showing increased charge transfer resistance (R_{ct}), consistent with reduced free calcium availability and the formation of electrochemically inactive complexes.

These findings position *Herniaria hirsuta* as a promising natural calcium chelator, useful for preventing scale in water systems. Its phytochemical interactions with metal ions support sustainable, eco-friendly solutions integrating local resources and modern electrochemical sensing, in line with green chemistry principles.

Conflicts of interest

The authors declare that there are no conflicts of interest, whether personal or financial, that might have impacted the findings or publication of this study.

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