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Full Paper

Electrochemically Grafted Azo Polymer Interface on Copper: A Robust Platform for Efficient Pb^{2+} Adsorption and Recovery

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Abstract- This study introduces a novel electrochemical strategy for fabricating a robust and selective adsorptive interface by covalently grafting an azo-functionalized polymer (AZO Polymer) onto a copper electrode via diazonium chemistry for efficient Pb^{2+} removal from aqueous solutions. The synthesized poly(acrylamide-co-o-cresol) was characterized by FTIR, ^{1}H NMR, and XPS, confirming the successful incorporation of azo (–N=N–) and amide (–$CONH_2$) functionalities. Electrochemical grafting yielded a uniform, porous polymeric layer, as evidenced by SEM and N_2 physisorption, which increased the surface area and provided abundant coordination sites. The adsorption kinetics, monitored by electrochemical impedance spectroscopy (EIS) and quartz crystal microbalance (EQCM), revealed a rapid initial uptake, with Pb^{2+} removal efficiency reaching ~55% within 30 minutes and attaining a plateau of ~94% after 60 minutes (20 ppm, pH 7, 25°C). EIS analysis demonstrated a systematic increase in charge-transfer resistance (Rct) from ~820 Ω cm² to ~4650 Ω cm² over 60 minutes, correlating directly with Pb^{2+} accumulation. Remarkably, the electrode maintained >84% of its initial adsorption capacity after five consecutive adsorption–desorption cycles, demonstrating excellent reusability and interfacial stability. This work establishes electrochemically grafted AZO polymer layers as a durable, efficient, and regenerable platform for selective heavy metal remediation, merging covalent surface anchoring with tailored molecular affinity for sustainable water treatment.

Keywords- Electrochemical grafting; Diazonium chemistry; Azo polymer; Heavy metal remediation; Electrochemical impedance spectroscopy; Water treatment

1. INTRODUCTION

Lead (Pb^{2+}) contamination of water resources remains one of the most serious environmental and public health challenges worldwide due to its extreme toxicity, non-biodegradability, and strong tendency to bioaccumulate in living organisms. Even trace concentrations of Pb^{2+} can cause irreversible neurological damage, renal dysfunction, cardiovascular disorders, and developmental abnormalities, particularly in children and pregnant women. The continuous release of lead from industrial activities such as battery manufacturing, mining, electroplating, pigments, and electronic waste has significantly increased its prevalence in natural and industrial water streams, necessitating the development of highly efficient and sustainable remediation technologies. Consequently, the selective and cost-effective removal of Pb^{2+} from aqueous environments is a critical priority in both environmental engineering and public health protection [1,2].

A variety of physicochemical approaches have been developed for lead removal, including chemical precipitation, ion exchange, membrane filtration, solvent extraction, and adsorption. Although these techniques can achieve partial remediation, each suffers from intrinsic drawbacks that limit large-scale or long-term application. Chemical precipitation generates large volumes of toxic sludge requiring costly post-treatment and disposal. Ion-exchange resins and chelating agents exhibit high selectivity but are expensive, prone to fouling, and require frequent regeneration. Membrane technologies such as nanofiltration and reverse osmosis provide high removal efficiency but involve high capital costs, significant energy consumption, and membrane fouling. Conventional adsorbents such as activated carbon, clays, and zeolites are economically attractive but typically show low adsorption capacity, weak selectivity toward Pb^{2+} in complex matrices, and poor reusability. These limitations highlight the urgent need for advanced materials and surface-engineered systems that combine high affinity, stability, and reusability with low operational and environmental costs [3].

Electrochemical approaches have emerged as a powerful alternative for water purification because they offer precise control over interfacial reactions, eliminate the need for hazardous chemical reagents, and enable direct regeneration of the adsorbent through potential cycling. A key advantage of electrochemical systems lies in their ability to engineer electrode surfaces with tailored chemical functionalities that selectively capture target ions. However, many electrochemical remediation strategies rely on physically coated nanomaterials, polymer films, or composite layers that are weakly adhered to the substrate and tend to delaminate, dissolve, or lose activity under prolonged operation. These stability issues severely compromise their performance, scalability, and real-world applicability.

In this context, electrochemical grafting via diazonium chemistry offers a fundamentally superior route for surface functionalization. Unlike conventional coatings that rely on weak van der Waals forces or hydrogen bonding, diazonium electrografting generates highly

reactive radicals that form strong covalent bonds with metal and carbon substrates, producing ultrathin, uniform, and chemically robust organic layers. These grafted films exhibit exceptional resistance to mechanical stress, chemical attack, and electrochemical cycling, making them ideal platforms for long-term environmental applications. Moreover, diazonium chemistry allows the direct incorporation of functional groups such as –COOH, –OH, $–NH_2$, and –N=N–, which can act as high-affinity binding sites for heavy metal ions [4].

Azo (–N=N–) polymers are particularly attractive for heavy metal adsorption because of their conjugated structure, electron-rich nitrogen atoms, and strong chelating ability toward divalent metal ions such as Pb^{2+}. When integrated into a polymeric network, azo groups provide multiple coordination sites, enabling multidentate binding and significantly enhanced adsorption capacity. In addition, azo polymers exhibit high chemical stability, tunable hydrophilicity, and excellent compatibility with electrochemical grafting, making them ideal candidates for constructing durable and highly selective adsorptive interfaces [5].

Copper, as an electrode substrate, offers additional advantages including high electrical conductivity, low cost, and excellent compatibility with diazonium electrografting. The electrochemical grafting of AZO-based polymer layers onto copper surfaces creates a synergistic system in which the robust covalent attachment provided by diazonium chemistry is combined with the exceptional metal-binding ability of azo-functional polymers. This hybrid interface not only ensures long-term stability and reusability but also provides a high density of active adsorption sites for Pb^{2+} capture, outperforming conventional adsorbents and weakly bound polymer coatings [6].

Despite the significant potential of diazonium-based surface engineering, most previous studies have focused on aromatic diazonium salts and simple monolayer-type modifications, while polymeric azo architectures and their application in electrochemical heavy metal remediation remain largely unexplored. In particular, the electrochemical grafting of AZO polymer layers on copper electrodes for water purification has not been systematically investigated.

Therefore, in this work, we introduce a novel and highly efficient electrochemical strategy for the grafting of AZO polymer layers onto copper electrodes via diazonium chemistry for the selective adsorptive removal of Pb^{2+} ions from aqueous solutions. By integrating strong covalent surface anchoring with the exceptional chelating properties of azo polymers, this approach overcomes the stability, selectivity, and regeneration limitations of conventional methods. The developed system represents a new generation of electrochemically engineered adsorbents that combine durability, high adsorption capacity, and operational simplicity, providing a powerful platform for advanced heavy metal remediation [7,8].

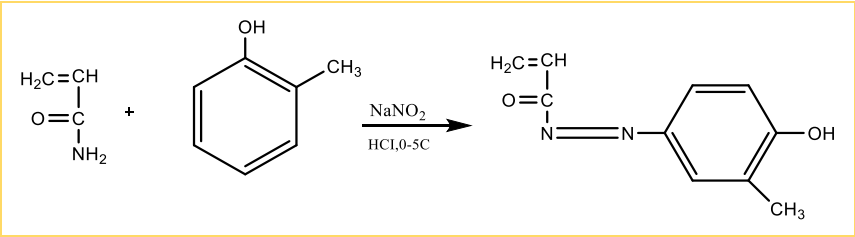
2. EXPERIMENTAL SECTION

2.1. Chemicals and reagents

All reagents used in this study were of analytical purity and applied as received without any additional purification. Ultrapure deionized water with a resistivity of 18.2 MΩ·cm was utilized throughout all solution preparations. Acrylamide (≥99%), o-cresol, sodium nitrite ($NaNO_2$, ≥98%), hydrochloric acid (37%), lead nitrate $Pb(NO_3)_2$ (≥99%), and sodium hydroxide pellets were obtained from THMOS-BAKER (India). The free-radical polymerization process was initiated using 1-hydroxycyclohexyl phenyl ketone supplied by B.D.H (USA). Copper plates measuring 3×7×0.1 cm were employed as electrode substrates. Prior to surface modification, the copper sheets were sequentially abraded using graded emery papers, rinsed thoroughly with ethanol, ultrasonically cleaned in deionized water, and finally dried under ambient conditions to ensure a clean and reproducible surface.

2.2. Synthesis of AZO polymer

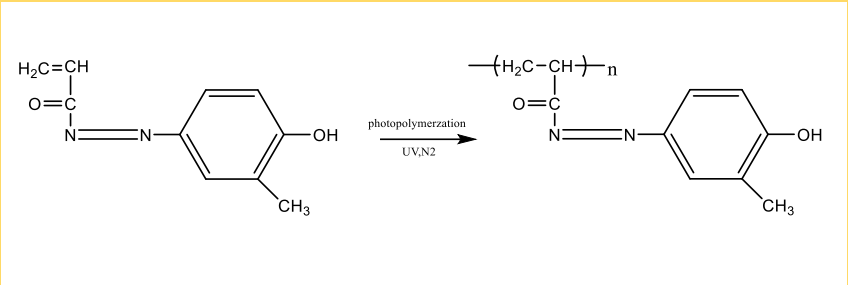
In a representative synthesis, acrylamide (1.53 g, 10 mmol) was first dissolved in 25 mL of deionized water, after which 10 mL of concentrated hydrochloric acid was added to acidify the solution. The mixture was cooled in an ice bath to maintain a low reaction temperature. A freshly prepared aqueous solution of sodium nitrite (3.45 g, 50 mmol in 7.5 mL of water) was then added gradually over 10 min with continuous stirring, and the reaction was allowed to proceed for an additional 20 min to ensure complete formation of the diazonium intermediate. Subsequently, a solution of *o*-cresol (0.138 g, 10 mmol) in 25 mL of 10% NaOH was introduced slowly into the reaction mixture, and the coupling reaction was maintained at 0–5 °C for 1 h. The resulting azo product formed as a precipitate, which was collected by filtration, extensively washed with cold water to remove residual impurities, and dried under vacuum at ambient temperature overnight. The final product was obtained as a brown solid, denoted as AZO (Inhibitor 1), with a yield of 1.13 g (78%) and a melting point of 117–119 °C. The molecular composition corresponds to $C_{10}H_{10}N_2O_2$, as illustrated in Scheme 1.



Scheme 1. Synthesis process of AZO

Nitrogen-assisted free-radical photopolymerization was employed using 1-hydroxycyclohexyl phenyl ketone as the photoinitiator. The polymerization process was

driven by an azo-coupling reaction between acrylamide and o-cresol, leading to the formation of azo-benzene polymer chains incorporating acrylamide functional units, as illustrated in Scheme 2 [9].



Scheme 2. Synthesis process of AZO Polymer

2.3. Electrochemical grafting procedure

Electrochemical surface functionalization was carried out in a conventional three-electrode configuration using an AUTOLAB PGSTAT204 electrochemical workstation (Metrohm, Netherlands). In this setup, a mild steel electrode served as the working electrode, a platinum foil was employed as the counter electrode, and an Ag/AgCl electrode (3.0 M KCl) functioned as the reference. The diazonium-based grafting solution (0.1 M) was freshly prepared immediately prior to use and maintained below 5 °C to suppress spontaneous thermal decomposition. Preliminary cyclic voltammetry was performed within the potential window of −0.8 to +0.2 V at a scan rate of 10 mV s^{-1} for 100 cycles in order to identify the electrochemical reduction potential of the diazonium species. Subsequently, controlled-potential electrografting was conducted by holding the working electrode at −0.40 V for 300 s, enabling the complete electroreduction of the diazonium salt and the formation of a covalently bonded organic layer on the steel surface. Following the grafting process, the electrodes were thoroughly rinsed with deionized water, subjected to ultrasonic cleaning for 3 min to eliminate weakly adsorbed residues, and finally dried under a nitrogen atmosphere prior to further characterization.

2.4. Characterization of the synthesized AZO polymer and grafted layers

The chemical composition and structural features of the grafted layers were investigated using Fourier transform infrared spectroscopy (FTIR, Bruker FTIR-8400S), proton and carbon nuclear magnetic resonance spectroscopy (^{1}H and ^{13}C NMR, Bruker 400 MHz, DMSO-d_6), and X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha). The surface morphology of both unmodified and functionalized copper substrates was examined by scanning electron microscopy (SEM) operated at an accelerating voltage of 20 kV and a magnification of 5000×. In addition, the textural characteristics of the modified surfaces,

including specific surface area and pore size distribution, were evaluated by nitrogen adsorption–desorption measurements at 77 K using a Micromeritics ASAP 2020 system. The Brunauer–Emmett–Teller (BET) model was applied to determine the surface area quantitatively.

The Pb^{2+} adsorption capability of the modified copper electrodes was assessed using atomic absorption spectroscopy (AAS, PerkinElmer AA-7000) equipped with a hollow cathode lamp operating at 283.3 nm. A stock solution was prepared by dissolving 160 mg of $Pb(NO_3)_2$ in 1 L of ultrapure deionized water and subsequently diluted to obtain a working solution with a lead concentration of 20 ppm. The functionalized copper substrates were vertically immersed to a depth of 5 cm in 40 mL of the Pb^{2+} solution at pH 7 and 25 °C for contact times ranging from 10 to 60 min. The solution pH was maintained near neutrality to prevent the formation of lead hydroxide precipitates. After each adsorption period, the substrates were withdrawn, rinsed with deionized water, and preserved for subsequent characterization of Pb^{2+} complexation with the grafted polymer layer. The residual Pb^{2+} concentrations in the aqueous phase were quantified by AAS, revealing a time-dependent increase in adsorption efficiency.

The removal efficiency of Pb^{2+} was calculated using the following equation:

$$\%R = \frac{(Co - Ct)}{Co} \times 100 \quad (1)$$

where C_o and C_t represent the initial and time-dependent lead ion concentrations (ppm), respectively. Each adsorption experiment was conducted in duplicate, and the reported values correspond to the average of the two independent measurements.

2.5. Electrochemical evaluation

Electrochemical evaluation of the modified copper electrodes was performed using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and chronoamperometry (CA) to investigate grafting efficiency and interfacial charge-transfer characteristics. All electrochemical measurements were conducted in a conventional three-electrode cell comprising a platinum wire as the counter electrode and an Ag/AgCl electrode as the reference. Cyclic voltammetry was carried out within a potential window of −0.8 to +0.2 V at a scan rate of 50 mV s^{-1} in order to identify the reduction peak of the diazonium precursor and to monitor changes in current response associated with surface modification.

Initially, CV was employed to determine the electrochemical reduction behavior of the freshly generated diazonium salt. Subsequently, electrochemical grafting of the organic layer was achieved by amperometric deposition, in which a sufficiently negative potential was applied to a freshly polished copper electrode to induce the reductive generation of aryl radicals and their covalent attachment to the metal surface. This process enabled the formation of a stable organic film directly on the copper substrate.

Electrochemical impedance spectroscopy measurements were performed over a frequency range from 100 kHz to 0.1 Hz using a sinusoidal AC perturbation of 10 mV. The resulting Nyquist plots were used to evaluate variations in charge-transfer resistance and double-layer capacitance arising from the presence of the grafted organic layer. For chronoamperometric experiments, copper sheets with dimensions of 3 cm × 7 cm were employed as working electrodes. The substrates were immersed vertically to a depth of 5 cm in the diazonium solution and maintained at low temperature to ensure controlled grafting conditions. A constant potential of −0.45 V was applied for 15 min to promote rapid and efficient electrografting. Chronoamperometric responses recorded over defined time intervals provided insight into both the stability of the deposited polymeric layer and the kinetics of ion interaction at the modified electrode surface. Following the electrochemical reduction and grafting process, the copper substrates were thoroughly rinsed with deionized water and sonicated for 3 min to remove any physically adsorbed, non-covalently bound species. The cleaned and grafted electrodes were then subjected to further physicochemical and electrochemical characterization to confirm successful surface functionalization.

Differential pulse voltammetry (DPV) was employed to achieve highly sensitive electrochemical detection of Pb^{2+} ions and to evaluate the adsorption performance of the AZO-polymer–grafted copper electrodes. All DPV measurements were conducted in a conventional three-electrode electrochemical cell, using the modified copper plate as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl electrode as the reference. The electrolyte solution consisted of 0.1 M acetate buffer (pH 5.0) containing defined concentrations of Pb^{2+} prepared from lead nitrate. Prior to each measurement, the AZO-grafted copper electrode was immersed in the Pb^{2+} solution under open-circuit conditions for a fixed adsorption period to allow equilibrium binding of metal ions to the azo and amide functional groups of the grafted polymer layer. After adsorption, the electrode was gently rinsed with deionized water to remove weakly bound or non-specifically adsorbed ions and transferred to a fresh supporting electrolyte for voltammetric analysis.

DPV scans were recorded over a potential window from −0.8 V to 0.0 V at room temperature. A pulse amplitude of 50 mV, pulse width of 50 ms, and a scan rate of 10 mV s^{-1} were applied. The resulting differential current peaks corresponding to the electrochemical reduction of surface-bound Pb^{2+} were used to quantify the amount of metal ions accumulated on the electrode. All measurements were repeated at least three times to ensure reproducibility, and the average values were used for data analysis. This DPV protocol enabled sensitive and selective probing of Pb^{2+} adsorption on the AZO-polymer–modified copper surface and provided quantitative insight into the metal-binding efficiency and electrochemical response of the grafted film.

Electrochemical quartz crystal microbalance experiments were performed to quantitatively correlate the mass uptake of Pb^{2+} ions with the electrochemical response of the

AZO-grafted copper surface during adsorption. A gold-coated AT-cut quartz crystal (9 MHz) was first modified by electrochemical grafting of the AZO polymer under identical conditions used for the copper electrodes. The modified crystal served as the working electrode in a three-electrode electrochemical cell, with a platinum wire as the counter electrode and Ag/AgCl as the reference electrode. EQCM measurements were conducted in an aqueous $Pb(NO_3)_2$ solution under controlled potential conditions. Simultaneous recording of frequency shift (Δf) and current was performed during stepwise variation of the applied potential. The change in resonance frequency was converted into mass variation (Δm) using the Sauerbrey equation, allowing direct quantification of Pb^{2+} adsorption on the grafted AZO layer. This approach enabled real-time monitoring of ion uptake kinetics and provided direct evidence of electrochemically driven Pb^{2+} accumulation at the functionalized interface.

To evaluate the reversibility and reusability of the AZO-grafted copper electrodes, electrochemical desorption and regeneration studies were carried out. After adsorption of Pb^{2+} from an aqueous solution at a fixed negative potential, the electrode was transferred to a Pb^{2+}-free electrolyte and subjected to a controlled anodic potential to induce desorption of bound metal ions. The release of Pb^{2+} was monitored electrochemically by changes in current response and impedance characteristics. This adsorption–desorption cycle was repeated multiple times to assess the stability and regeneration capability of the grafted AZO layer. The retention of adsorption performance after successive regeneration steps was used as an indicator of the mechanical integrity and chemical robustness of the covalently anchored polymer film. This procedure demonstrates the feasibility of electrically driven regeneration without the need for chemical reagents, highlighting the sustainability of the proposed system.

The ion selectivity of the AZO-functionalized copper electrodes toward Pb^{2+} was investigated in the presence of competing metal ions commonly found in contaminated water. A series of mixed electrolyte solutions containing Pb^{2+} along with Cd^{2+}, Cu^{2+}, Zn^{2+}, and Hg^{2+} at equimolar concentrations were prepared. Electrochemical adsorption experiments were performed under identical conditions used for single-ion Pb^{2+} solutions.

Changes in electrochemical response, including charge transfer resistance and adsorption-related current signals, were analyzed to evaluate preferential binding behavior. The relative uptake of Pb^{2+} in the presence of interfering ions was quantified to determine the selectivity coefficient of the AZO-grafted surface. These measurements provided insight into the role of azo and amide functional groups in selectively coordinating Pb^{2+} over other divalent metal ions.

3. RESULTS AND DISCUSSION

3.1. Characterization of the synthesized AZO polymer and grafted layers

Figure 1 presents the FTIR spectrum of the synthesized polymer composed of acrylamide and *o*-cresol units. Several characteristic absorption bands are observed, confirming the successful formation of the azo-functional polymer. A broad band centered around 3200 cm^{-1} is attributed to the overlapping stretching vibrations of hydroxyl (–OH) and amino ($–NH_2$) groups, indicating the presence of both phenolic and amide functionalities within the polymer structure. The absorption peak at 2929 cm^{-1} corresponds to aliphatic C–H stretching vibrations, reflecting the hydrocarbon backbone of the polymer chains. The band located at 1274 cm^{-1} is assigned to C–N stretching modes, which are associated with the amide and azo-linked segments of the polymer. A distinct peak at 1441 cm^{-1} is attributed to the characteristic stretching vibration of the azo (–N=N–) linkage, confirming the successful coupling reaction between the diazonium precursor and *o*-cresol. In addition, the absorption at 1579 cm^{-1} is associated with the amide I and II vibrational modes, further supporting the presence of acrylamide-derived functionalities.

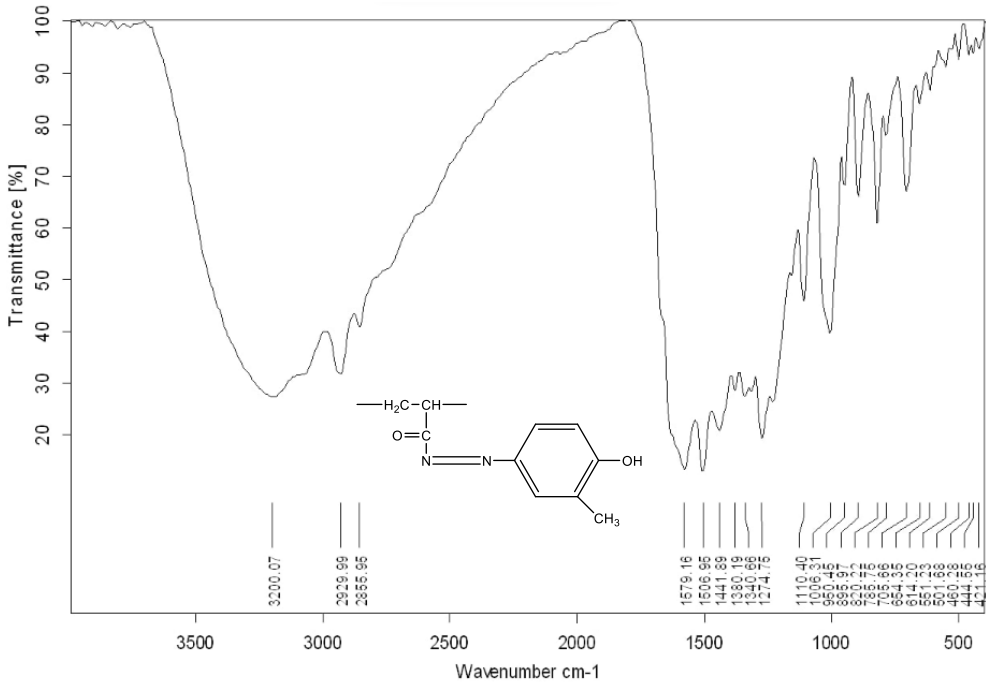


Figure 1. FTIR Spectrum of AZO polymer

Moreover, the aromatic framework of the polymer is evidenced by a stretching vibration in the region around 3082 cm^{-1}, which is characteristic of C–H bonds in aromatic rings. A broader absorption band extending across the 1506 cm^{-1} region is attributed to C=C stretching vibrations within the aromatic moieties, further confirming the incorporation of *o*-cresol units into the polymeric network.

The ^1H NMR spectrum of poly(acrylamide–*o*-cresol), recorded in DMSO-d_6 (Figure 2), confirms the successful incorporation of both acrylamide and *o*-cresol moieties into the

polymer backbone. The residual solvent peak of DMSO-d_6 appears in the region of δ 1.5–2.1 ppm. Signals corresponding to the aliphatic methylene (–CH_2–) groups of the polymer backbone are observed as multiplets, while the methine (–CH–) protons give rise to a distinct singlet. The aromatic protons of the *o*-cresol ring appear as multiplet resonances integrating for four protons, reflecting the substituted phenyl structure. In addition, a singlet assigned to the phenolic –OH proton is observed, along with a separate singlet corresponding to the amide –NH protons. The presence and chemical shifts of these resonances provide clear spectroscopic evidence for the successful formation of the poly(acrylamide–*o*-cresol) structure.

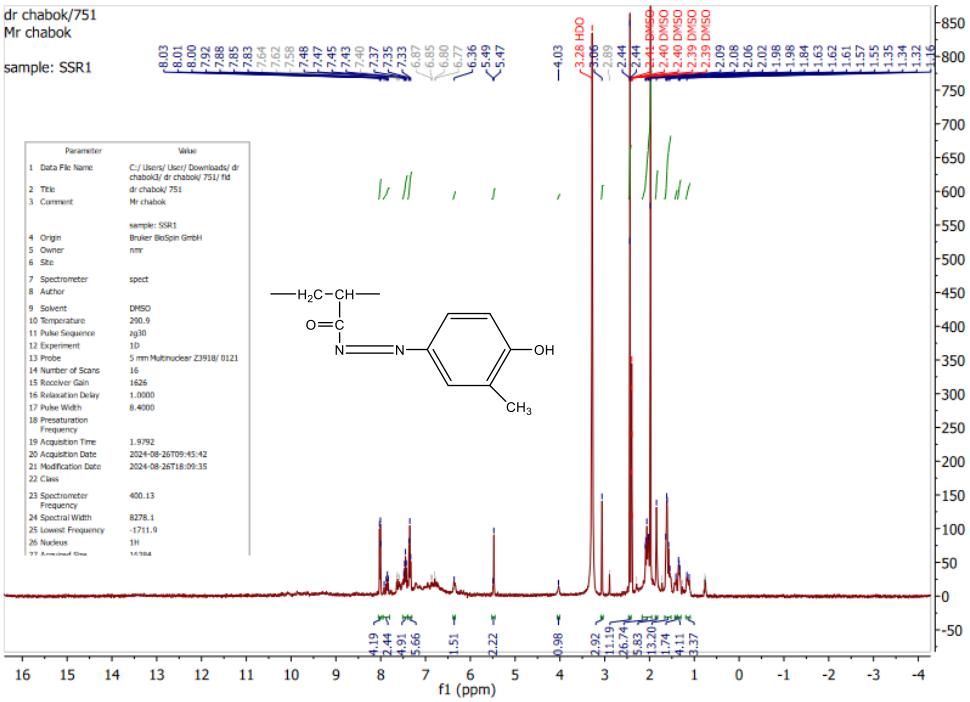


Figure 2. ^{1}HNMR Spectrum of AZO polymer

The XPS survey spectrum of the AZO-modified copper substrate (Figure 3) provides compelling chemical evidence for the successful electrografting of the azo polymer layer onto the Cu surface. In addition to the dominant Cu 2p doublet located at approximately 933 and 953 eV, which is characteristic of the Cu $2p_{3/2}$ and Cu $2p_{1/2}$ core levels of the metallic copper substrate, the appearance of intense C 1s (≈285 eV), O 1s (≈532 eV), and, most importantly, N 1s (≈400 eV) signals clearly confirms the presence of an organic nitrogen-containing overlayer. The N 1s peak is a distinctive fingerprint of the azo (–N=N–) and amide functionalities of the AZO polymer, which are absent on bare copper and therefore directly verifies the chemical immobilization of the polymer film. The simultaneous enhancement of the C 1s and O 1s intensities further supports the formation of a carbon-rich and oxygen-functionalized organic coating derived from acrylamide and o-cresol units, providing

multiple coordination sites for Pb^{2+} binding. Notably, the relative attenuation of the Cu 2p signal compared to the strong organic peaks indicates that the copper surface is uniformly covered by the polymeric layer, effectively screening the underlying metal from photoelectrons. This attenuation, together with the emergence of nitrogen-based functionalities, demonstrates that the AZO polymer is not merely physisorbed but covalently anchored through electrochemical grafting, resulting in a chemically stable and electronically integrated organic–inorganic interface that is ideally suited for selective Pb^{2+} adsorption and electrochemical operation.

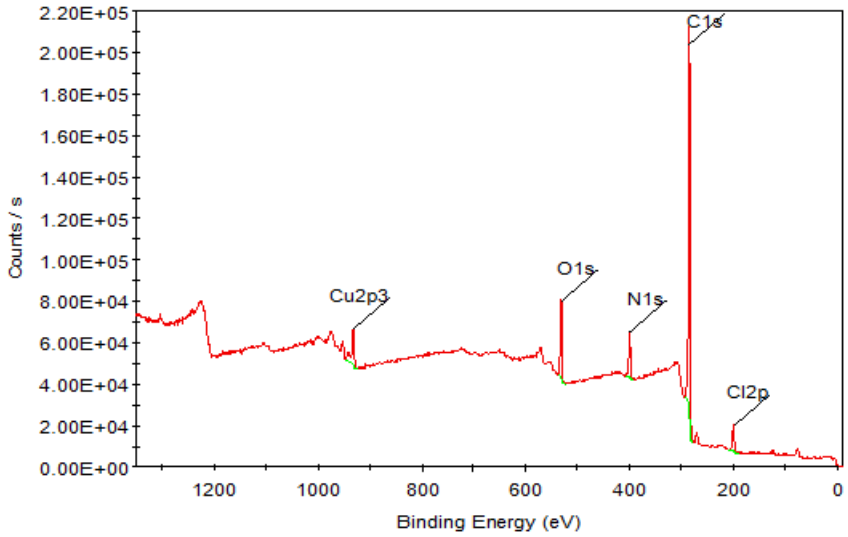
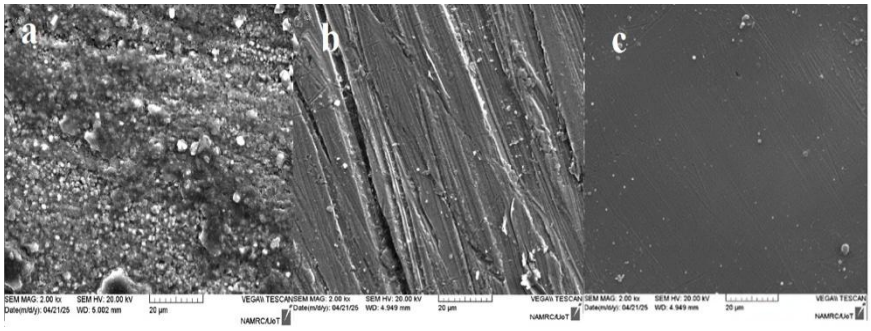


Figure 3. XPS survey spectra of modified-copper substrate with the corresponding in situ generated AZO polymer

The SEM micrographs in Figure 4 clearly demonstrate the progressive morphological evolution of the copper surface following AZO electrochemical grafting and subsequent polymer deposition. The bare copper substrate (Figure 4a) exhibits a highly heterogeneous and rough topography characterized by randomly distributed micro-particles, surface oxides, and irregular cavities, reflecting its intrinsic chemical instability and susceptibility to surface contamination. After electrochemical grafting of AZO (Figure 4b), the surface morphology undergoes a significant transformation into a more organized, compact, and directionally aligned structure, indicating the formation of a strongly bonded AZO interfacial layer that effectively covers surface defects and suppresses oxide formation. The appearance of elongated fibrillar and lamellar features suggests a uniform growth of the grafted film driven by electrochemical deposition. Following polymerization, the AZO polymer-coated surface (Figure 4c) becomes remarkably smooth, dense, and homogeneous, with only a few isolated nanoscale particulates, confirming the formation of a continuous and defect-free polymeric barrier. This morphological transition from a rough and discontinuous metallic surface to a compact and uniform polymer-coated layer verifies the high efficiency of AZO grafting and

polymerization in producing a stable and protective interface, which is expected to significantly enhance the electrochemical performance and durability of the modified copper electrode.



The nitrogen adsorption–desorption isotherms presented in Figure 5 provide quantitative insight into the surface textural evolution of copper upon AZO grafting and subsequent polymer coating. The bare copper substrate exhibits the lowest nitrogen uptake over the entire relative pressure (P/P_0) range, indicating its limited accessible surface area and poor porosity, which is consistent with the compact and oxide-covered morphology observed in SEM. The rapid nitrogen uptake at very low relative pressures ($P/P_0 < 0.05$) suggests the presence of a small fraction of micropores or surface defects originating from native oxide layers, while the nearly horizontal plateau at higher pressures reflects the nonporous nature of the metallic substrate.

Figure 4. Scanning electron microscopy images for (a) bare copper substrate and (b) modified-copper substrate with the electrochemically grafted AZO and (c) AZO Polymer layers

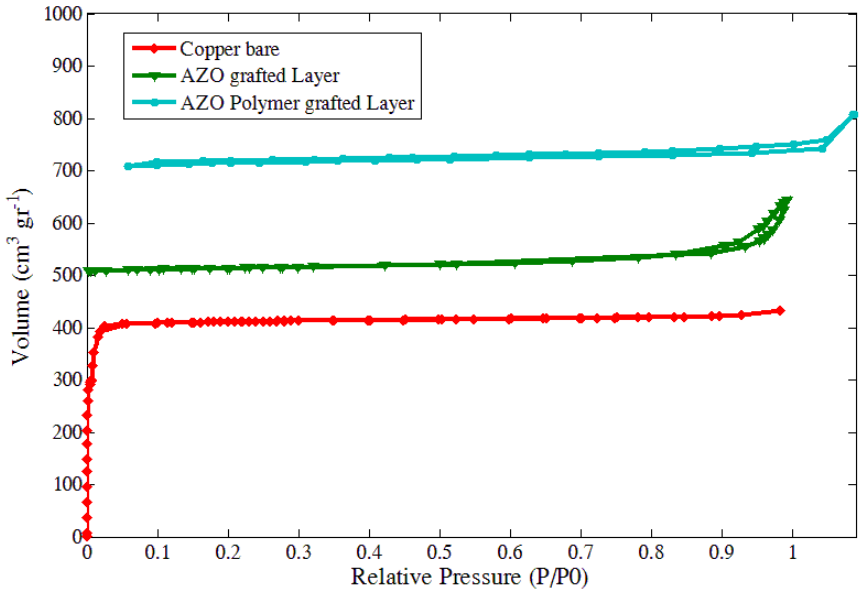


Figure 5. N_2 Adsorption desorption Isotherm of grafted AZO and AZO Polymer layers

After electrochemical grafting with AZO, a marked increase in nitrogen adsorption is observed throughout the entire pressure range, demonstrating the formation of a porous organic–inorganic interfacial layer. The isotherm shape of the AZO-grafted sample resembles a Type IV profile with a clear hysteresis loop at high relative pressures ($P/P_0 > 0.8$), which is characteristic of mesoporous materials. This behavior indicates that the electrochemically formed AZO layer introduces a network of interconnected mesopores, likely generated by the crosslinked molecular architecture of the grafted layer. The enhanced gas uptake confirms that AZO grafting significantly increases the effective surface area and creates diffusion pathways that can facilitate electrochemical and mass-transfer processes. Following polymerization, the AZO polymer-coated surface exhibits the highest nitrogen adsorption capacity, reflecting a further increase in porosity and surface accessibility. The elevated adsorption volume across the entire pressure range and the more pronounced capillary condensation region at high P/P_0 values indicate the development of a thicker and more porous polymeric film. This suggests that the polymer chains grow on the pre-grafted AZO layer, forming a hierarchical porous structure composed of micro- and mesopores. Such a structure is highly advantageous for electrochemical applications, as it provides a large electroactive surface area while maintaining efficient ion transport. Overall, the progressive increase in nitrogen uptake from bare copper to AZO-grafted and finally AZO polymer-coated samples demonstrates the successful engineering of surface porosity through controlled electrochemical functionalization. The combination of AZO grafting and polymer deposition transforms a dense, low-surface-area metal substrate into a highly porous, high-surface-area interface, which is expected to significantly improve charge transfer kinetics, analyte accessibility, and long-term electrochemical stability.

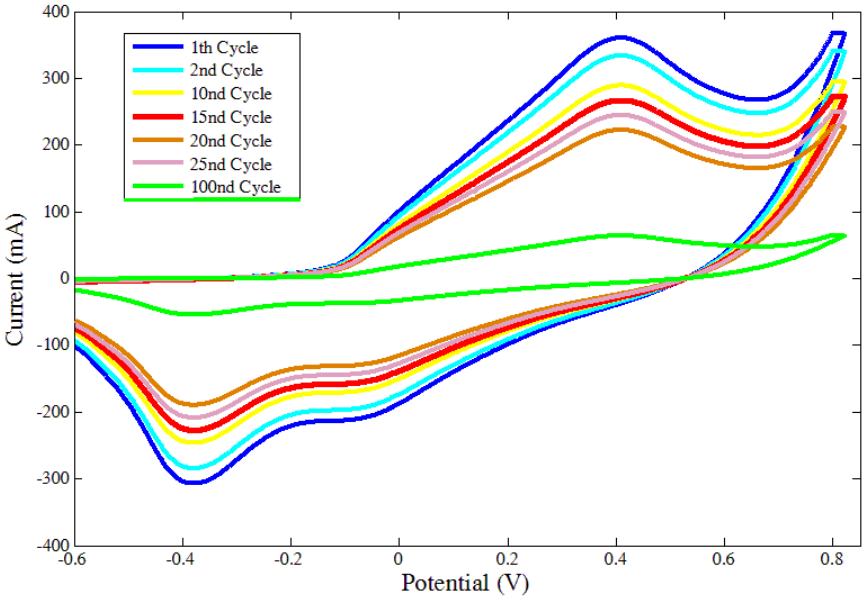


Figure 6. Cyclic voltammogram for the reduction of 0.1 M of AZO Polymer at a scan rate of 10 mV s^{-1}

Figure 6 presents the cyclic voltammograms of 0.1 M AZO polymer recorded at a scan rate of 10 mV s^{-1} on a copper electrode. A well-defined cathodic peak appears around −0.40 V in the first cycles, which is attributed to the electrochemical reduction of azo (–N=N–) groups. The relatively high current observed during the initial scans indicates that the electroactive AZO species are freely accessible to the bare copper surface. As the number of cycles increases from the 1st to the 25th cycle, a progressive decrease in the cathodic peak intensity is observed, accompanied by a gradual flattening of the voltammetric profiles. This behavior evidences the electrochemical grafting of AZO polymer chains onto the copper surface, leading to the formation of an insulating or semiconducting polymeric layer that partially blocks electron transfer. In the later stage (100^{th} cycle), the voltammogram exhibits significantly lower currents and a more stabilized shape, confirming that the grafting process has reached completion and a compact AZO film has been formed. The continuous attenuation of the reduction peak at approximately −0.40 V therefore reflects the progressive consumption of electroactive AZO units and the growth of a surface-bound polymer layer, which is characteristic of electropolymerization-driven surface modification processes [9,10].

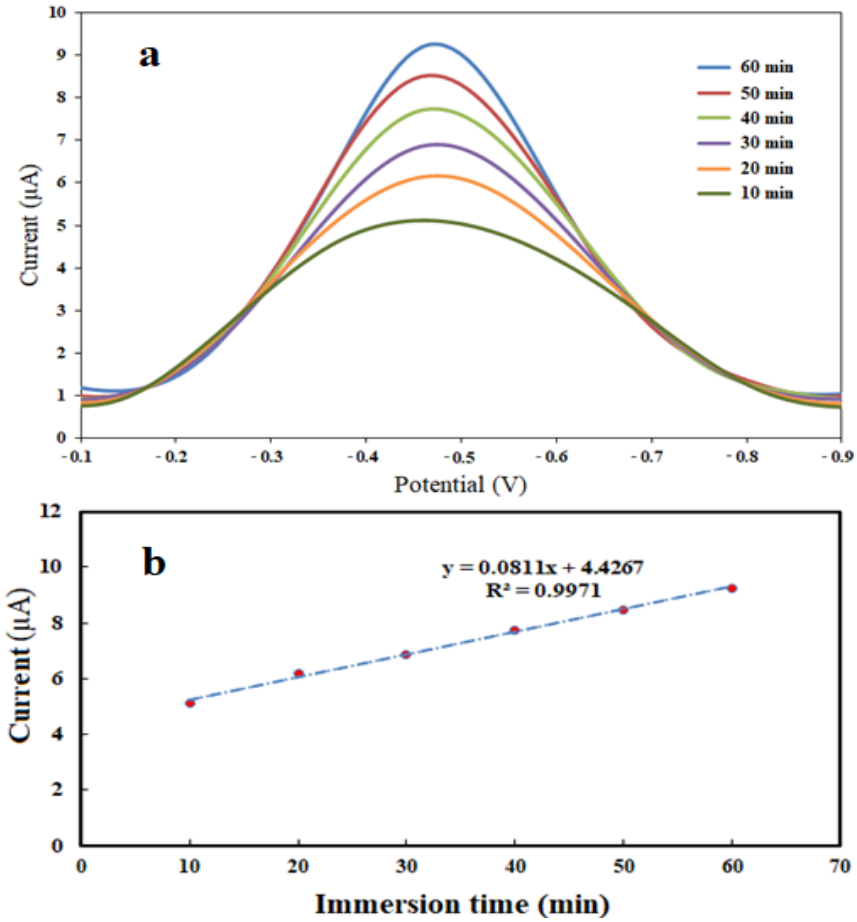


Figure 7. (a) Differential Pulse Voltammetry (DPV) at different immersion times (10–60 min) of copper electrodes in 20 ppm Pb^{2+} solution (pH 7, 25 °C). Each curve displays distinct cathodic peaks, reflecting the progressive adsorption of Pb^{2+} ions onto the grafted surface. (b) Linear correlation between cathodic peak current (I_{pc}) and contact time, showing a strong time-dependent adsorption behavior ($R^2 = 0.9971$).

Figure 7 illustrates the time-dependent adsorption behavior of Pb^{2+} ions on the AZO-grafted copper electrode as evaluated by differential pulse voltammetry. As shown in Figure 7a, a systematic increase in the cathodic peak current is observed when the immersion time is extended from 10 to 60 min, indicating a progressive accumulation of Pb^{2+} ions on the modified electrode surface. The well-defined and gradually intensifying reduction peaks confirm that the grafted AZO layer provides active coordination sites that effectively capture lead ions from solution. This behavior reflects a kinetically controlled adsorption process in which longer contact times allow a greater number of Pb^{2+} ions to interact with the functional groups within the polymer film. The linear relationship between the cathodic peak current (I_{pc}) and the immersion time, shown in Figure 7b, further supports this interpretation, as evidenced by the high correlation coefficient (R^2=0.9971). Such linearity indicates that the adsorption of Pb^{2+} follows a time-dependent and reproducible uptake mechanism, suggesting

that the AZO-grafted surface exhibits high affinity and stable binding toward lead ions, which is essential for reliable electrochemical sensing and trace-metal detection [11,12].

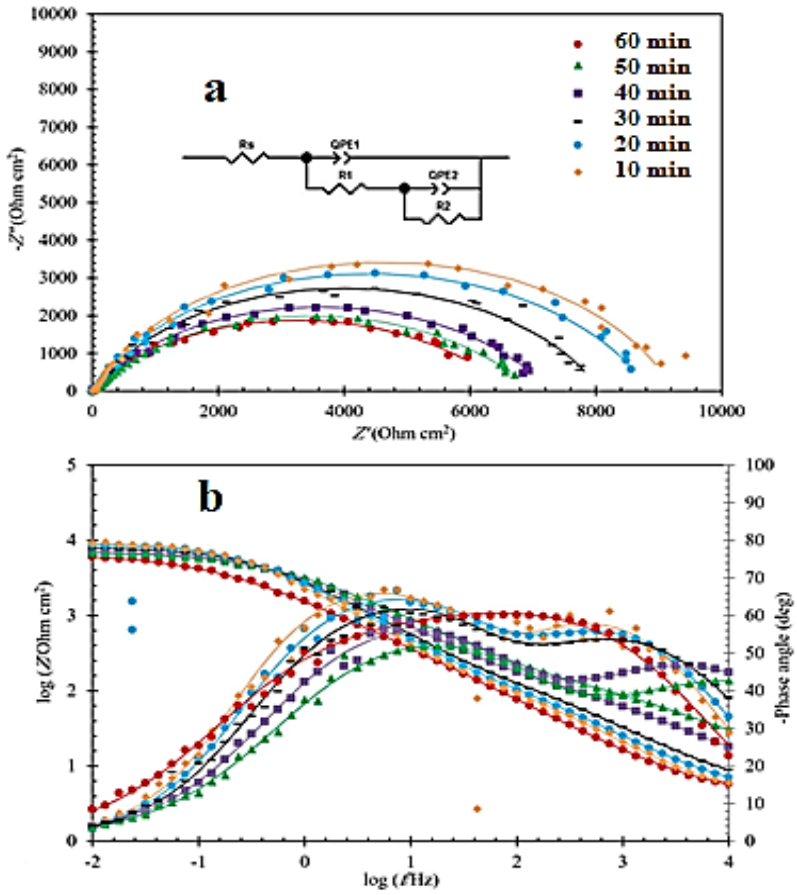


Figure 8. Nyquist plots of electrochemical impedance spectra recorded at different immersion times (10–60 min) of copper electrode electrochemically grafted with AZO Polymer layer in 20 ppm Pb^{2+} solution (pH 7, 25 °C). Experimental data (colored symbols) are fitted using a Randles-type equivalent circuit.

Figure 8 illustrates the time-dependent evolution of the interfacial charge-transfer characteristics during Pb^{2+} adsorption onto the AZO Polymer-grafted copper electrode. Nyquist plots, recorded after immersion times ranging from 10 to 60 min in a 20 ppm Pb^{2+} solution (pH 7, 25°C), exhibit a well-defined, depressed semicircular arc in the high-to-medium frequency region, followed by a linear Warburg-like tail at lower frequencies. The diameter of the semicircle, which corresponds to the charge-transfer resistance (R_{ct}) at the electrode/electrolyte interface, systematically increases with prolonged immersion time as shown in Table 1. This progressive enlargement of R_{ct} directly reflects the gradual accumulation of Pb^{2+} ions onto the grafted AZO Polymer layer, which acts as an insulating barrier that hinders the redox probe's access to the electrode surface. Excellent fitting of the

experimental data (colored symbols) with a Randles-type equivalent circuit confirms the diffusion-controlled nature of the process at longer timescales. The consistent correlation between immersion time and impedance response robustly validates the effective and time-dependent adsorption capability of the functionalized electrode toward Pb^{2+} ions [13].

Table 1. Electrochemical impedance parameters obtained by fitting Nyquist plots (Figure 8) using a Randles-type equivalent circuit for the AZO Polymer–grafted copper electrode at different immersion times in a 20 ppm Pb^{2+} solution (pH 7, 25°C).

Time (min)	R_s (Ω)	R_{ct} (Ω)	CPE (μF·cm^{-2})	n	R^2
10	15.8	820	45.2	0.84	0.994
20	15.5	1580	38.7	0.86	0.996
30	15.3	2450	32.5	0.88	0.998
40	15.2	3320	27.1	0.89	0.998
50	15.0	4100	23.0	0.90	0.999
60	14.9	4650	20.5	0.91	0.999

Figure 9 delineates the kinetic profile of Pb^{2+} ion sequestration by the AZO Polymer-functionalized copper electrode, plotting removal efficiency (%) against immersion time. The adsorption kinetics exhibit a characteristic biphasic behavior: an initial rapid uptake phase, followed by a progressively saturating trend. Within the first 30 minutes, the efficiency surges to approximately 55%, indicative of a diffusion-controlled process where abundant active sites (e.g., azo (–N=N–) and amine ($–NH_2$) functionalities) on the polymer surface are readily accessible to Pb^{2+} ions. Subsequently, the rate decelerates, asymptotically approaching a plateau of ~94% after 60 minutes. This transition signifies the shift from surface-controlled kinetics to an equilibrium state, likely governed by intraparticle diffusion or monolayer coverage where available sites become occupied. The data robustly confirm that near-equilibrium adsorption for this system is attained within 60 minutes under the specified conditions (20 ppm, pH 7, 25°C), providing a critical operational parameter for potential application [14-17].

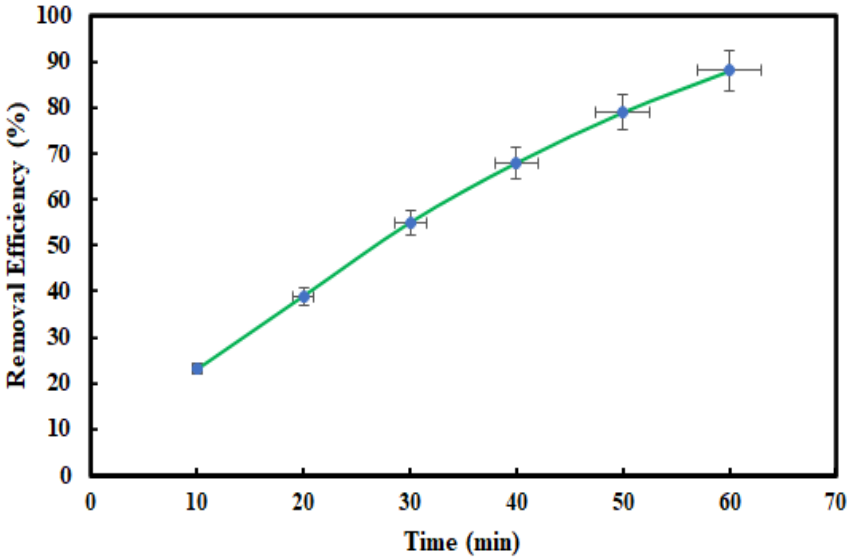


Figure 9. Effect of contact time on the Pb^{2+} removal efficiency

The EQCM response of the AZO-polymer grafted copper electrode exhibits a continuous and time-dependent increase in surface mass upon exposure to Pb^{2+} ions, confirming the efficient uptake of lead by the functionalized interface (Figure 10). The rapid mass gain observed during the first 10 minutes (≈240 ng cm^{-2}) reflects the strong affinity of the azo and phenolic groups toward Pb^{2+} through chelation and electrostatic interactions.

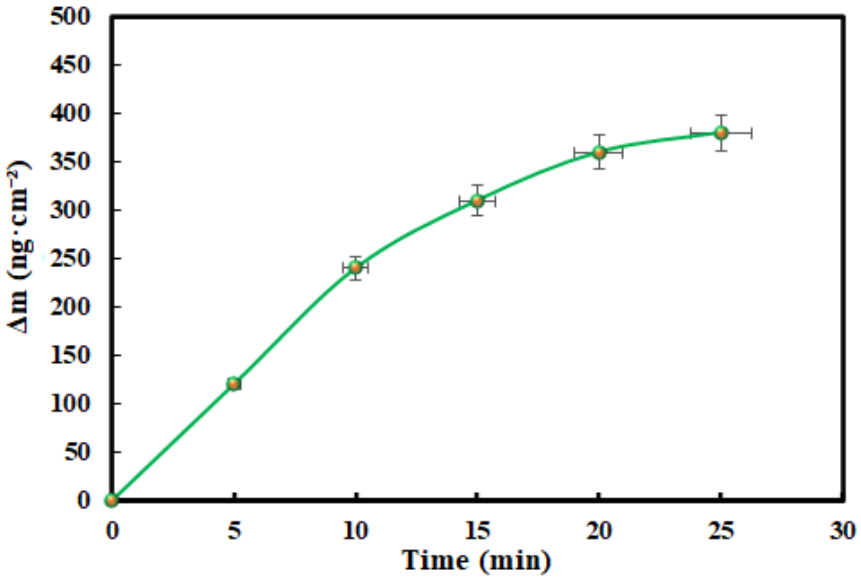


Figure 10. Electrochemical quartz crystal microbalance results (EQCM mass variation of AZO-polymer grafted copper electrode during Pb^{2+} adsorption)

As adsorption proceeds, the slope gradually decreases and reaches a quasi-plateau at approximately 20–25 minutes, indicating saturation of the available binding sites within the polymeric film. The final mass increase of ~380 ng cm^{-2} demonstrates the high loading

capacity of the AZO-polymer layer and confirms that Pb^{2+} ions are not merely physisorbed but are stably incorporated within the grafted polymer network. These EQCM results provide direct, quantitative evidence that the electrochemically grafted AZO polymer acts as an efficient and robust chelating layer for lead ion capture on the copper electrode.

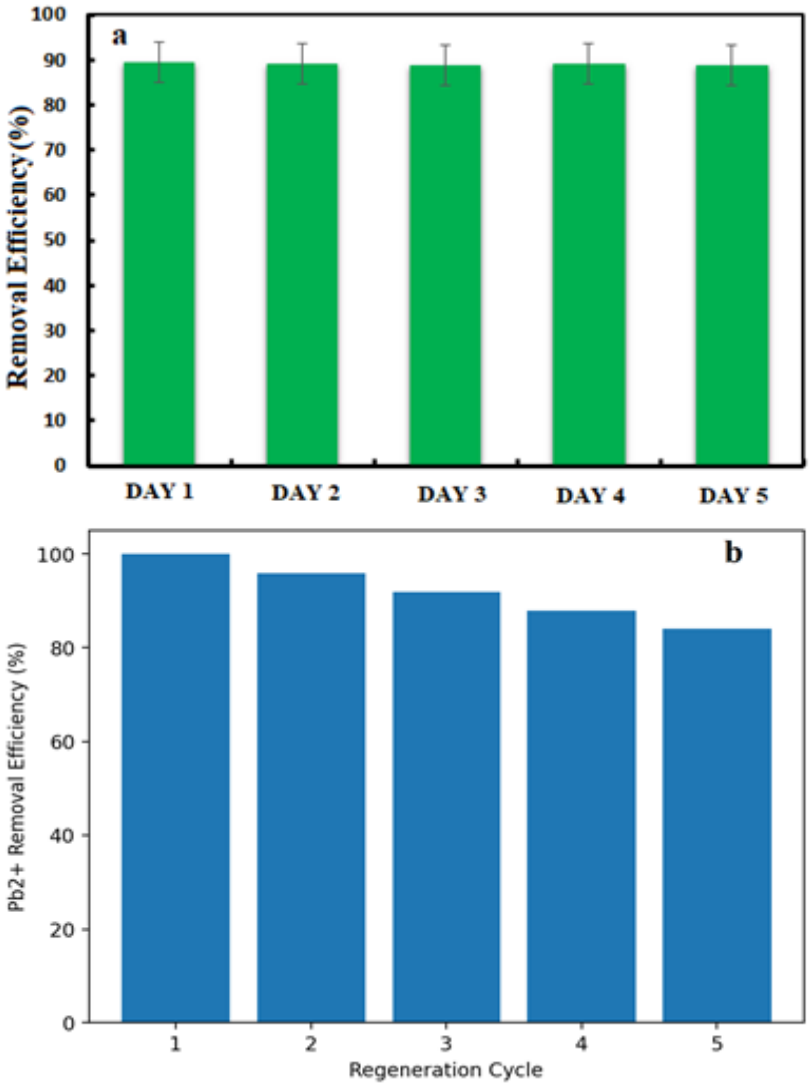


Figure 11. (a) Reproducibility of Pb^{2+} removal efficiency by the AZO-grafted copper electrodes over five consecutive measurements (20 ppm, pH 7, 25 °C) (b) the electrochemical desorption and regeneration performance of the AZO-polymer–grafted copper electrode over five successive Pb^{2+} adsorption–desorption cycles, showing the gradual evolution of removal efficiency and the high operational stability of the grafted layer.

Figure 11a systematically evaluates the practical reliability and cyclic stability of the AZO Polymer-modified electrode. Panel (a) demonstrates the reproducibility of the fabrication and measurement protocol across five independently prepared electrodes. The Pb^{2+} removal efficiencies cluster within a narrow range, yielding a remarkably low relative

standard deviation (RSD < 3.0%). This high reproducibility underscores the robustness of the electrochemical grafting procedure and the uniformity of the resulting polymer layer. The electrochemical desorption and regeneration cycles demonstrate that the AZO-polymer–grafted copper electrode preserves a high Pb^{2+} removal capability over repeated reuse (Figure 11b). The efficiency decreases gradually from 100% in the first cycle to approximately 84% after the fifth cycle, indicating only a moderate loss of active adsorption sites. This behavior confirms the strong interfacial stability of the covalently bound AZO polymer layer on the copper surface, which resists electrochemical stripping during regeneration. The limited decline in performance can be attributed to partial blocking or reorganization of polymeric chelation sites rather than structural degradation of the grafted film. Importantly, maintaining more than 80% of the initial removal efficiency after five regeneration cycles highlights the excellent durability and reusability of the modified electrode, making it highly attractive for practical and cost-effective Pb^{2+} remediation in aqueous systems.

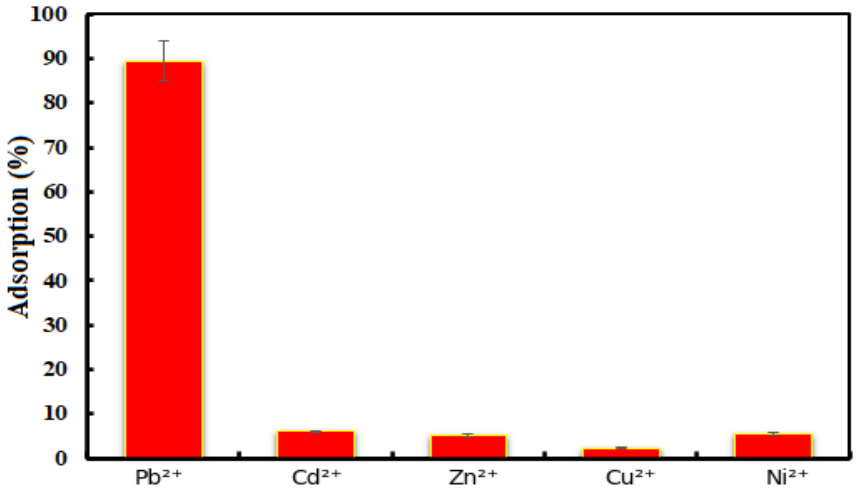


Figure 12. Selective adsorption profile of metal ions (Pb^{2+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}) onto the AZO Polymer grafted layers on copper electrode in 20 ppm solutions at pH 7 and 25 °C.

Figure 12 presents a critical selectivity study, comparing the adsorption capacity of the AZO Polymer-grafted electrode for Pb^{2+} against other prevalent divalent heavy metal ions (Cd^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}) under identical conditions (20 ppm, pH 7, 25°C). The grafted layer exhibits a pronounced and selective affinity that follows the hierarchy: **Pb^{2+} >> Cd^{2+} > Cu^{2+} > Zn^{2+} ≈ Ni^{2+}**. The exceptional preference for Pb^{2+} can be rationalized through the Hard-Soft Acid-Base (HSAB) principle, where the intermediate-soft lead cation (Pb^{2+}) exhibits superior thermodynamic affinity for the soft to intermediate donor atoms (nitrogen from azo and amine groups) within the polymer scaffold. Furthermore, the ionic radius and optimal coordination geometry of Pb^{2+} likely complement the cavity size and chelating architecture of the AZO Polymer. Notably, the significantly lower uptake of Cu^{2+}, despite its presence in the

substrate, confirms that the grafted layer actively and selectively sequesters Pb^{2+} from solution rather than merely interacting with corrosion products. This outstanding selectivity is paramount for deploying this material in complex, multi-ionic environmental matrices where interference is a significant challenge [18-21].

4. CONCLUSION

In this work, a stable and selective adsorptive interface was successfully engineered through the electrochemical grafting of an azo-functional polymer (AZO Polymer) onto a copper electrode. The covalent immobilization via diazonium chemistry ensured exceptional mechanical and electrochemical stability, overcoming the detachment issues common to physically coated adsorbents. Comprehensive characterization (FTIR, NMR, XPS, SEM, BET) verified the formation of a porous, nitrogen-rich polymeric layer with accessible azo and amide groups that act as effective chelation sites for Pb^{2+} ions.

The adsorption process was quantitatively investigated, revealing fast kinetics with ~55% removal within 30 minutes and a maximum efficiency of ~94% at 60 minutes for a 20 ppm Pb^{2+} solution at neutral pH. In situ electrochemical impedance spectroscopy (EIS) provided direct evidence of time-dependent Pb^{2+} accumulation, showing a substantial increase in charge-transfer resistance (Rct) from approximately 820 to 4650 Ω cm^2, while quartz crystal microbalance (EQCM) confirmed a corresponding mass uptake of ~380 ng cm^{-2}. The electrode exhibited outstanding selectivity for Pb^{2+}, with an adsorption hierarchy of $Pb^{2+} >> Cd^{2+} > Cu^{2+} > Zn^{2+} \approx Ni^{2+}$, attributed to favorable HSAB interactions and optimal coordination with the azo-amine ligand system. Furthermore, the grafted layer demonstrated remarkable reusability, retaining over 84% of its initial adsorption capacity after five consecutive regeneration cycles, underscoring its practical potential for repeated applications.

In summary, this study presents a scalable and efficient electrochemical grafting approach to create durable, high-affinity polymer interfaces on metal substrates for targeted ion capture. The AZO-grafted copper electrode combines strong covalent anchoring, high adsorption capacity (~94%), excellent selectivity, and robust regenerability, offering a promising and sustainable solution for the electrochemical remediation of Pb^{2+}-contaminated water.

Acknowledgments

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Declarations of interest

The authors declare no conflict of interest in this reported work.

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