

Highly efficient magnetic iron oxides-polyaniline nanocomposite for electrochemical removal of lead and cadmium ions from contaminated water

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ABSTRACT

Background: This study presents the first successful cyclic voltammetry-assisted one-step electrochemical synthesis of polyaniline-iron oxide nanocomposites. The composite films were developed by reducing an iron-triethanolamine complex in an alkaline solution containing aniline monomers, enabling the uniform integration of iron oxide nanoparticles into a conductive polyaniline matrix.

Methods: The nanocomposites were synthesized through electrodeposition, and characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier-transform infrared spectroscopy (FTIR). Thermal stability was evaluated using thermogravimetric (TGA) and differential thermal analysis (DTA).

Significant Findings: The synthesized nanocomposites exhibited excellent capabilities for adsorption or uptake lead and cadmium ions from water, following a chemisorption mechanism as suggested by kinetic and isotherm modeling. The materials demonstrated high reusability with negligible loss in adsorption efficiency over three consecutive adsorption-desorption cycles, and good repeatability with consistent adsorption capacities across multiple batches. Maximum adsorption capacities reached 96.99 mg/g for cadmium and 335.57 mg/g for lead, surpassing many reported materials. This work highlights a scalable electrochemical approach for fabricating high-performance nanocomposite adsorbents for water purification.

1. Introduction

Because of its reducing capabilities, bulk iron oxide has a strong potential to decompose hazardous substances in aqueous media [1]. Iron oxide nanoparticles, due to their large surface area, exhibit superior efficiency in wastewater treatment compared to bulk materials, facilitating heavy metal removal from solutions [2–6].

Several synthesis methods for magnetic iron oxides have been reported, including hydrothermal [7], microemulsion [8], sonochemical [9], laser pyrolysis [10], microbial synthesis [11,12], and electrochemical approaches [6,13,14]. Among these, electrochemical synthesis stands out as a low-cost, scalable, and controllable technique, offering safe and reproducible deposition of iron oxide thin films under adjustable conditions such as voltage, current, pH, and temperature. Recently,

there has been growing interest in hybrid composites combining conductive polymers and metal oxides, merging magnetic and conductive properties for applications in corrosion protection, electrocatalysis, and energy devices [15–18]. These composites are also attractive for environmental remediation due to their high surface area and magnetic properties [19]. Recently, sol-gel synthesized magnetic nanocomposites have shown promising performance in heavy metal removal. Using one-pot strategies, spinel iron oxide nanoparticles confined within porous silica matrices exhibited high surface areas and effective Cd(II) adsorption following Langmuir isotherm behavior. These findings emphasize the importance of nanostructured materials for enhancing adsorption efficiency in environmental applications [20].

Polypyrrole [21–23], polyaniline [24–26], and polythiophenes [27–29] have been widely explored for integration with iron oxides,

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producing multifunctional nanocomposites. Polyaniline (PANI) is particularly promising due to its doping flexibility, environmental stability, and low cost. PANI-iron oxide composites can be synthesized by chemical or electrochemical methods [25,26,30,31], with electropolymerization being advantageous for simplicity and effectiveness. While iron oxides have been synthesized from alkaline media via triethanolamine (TEA) complexation, simultaneous electrochemical deposition of PANI and iron oxides from basic media remains unexplored.

Heavy metals like cadmium (Cd^{2+}) and lead (Pb^{2+}) are persistent, bioaccumulative, and highly toxic. Cadmium adversely affects cells, kidneys, bones, and lungs [32], while lead disrupts brain development, damages kidneys, and can cross the blood-brain barrier, causing severe neurotoxic effects [33]. Both metals are frequently found near hazardous waste sites, with WHO setting very low permissible limits for drinking water. Thus, efficient removal strategies for Cd and Pb ions are critically needed. Technologies including adsorption [34], flotation [35], ion exchange [36], coagulation [37], reverse osmosis, nanofiltration [38], electrolysis [39], and biosorption [40] have been utilized. Metal hydroxide precipitation by pH adjustment is common but generates large volumes of sludge. Biological methods are promising yet complicated by soil chemistry [41]. Activated carbon, despite being effective, poses separation challenges after treatment [42]. Magnetic materials with surface functionalization have demonstrated high Pb^{2+} and Cd^{2+} uptake capacities [6,43], especially those with high saturation magnetization [44].

In this work, we found that the simultaneous electrochemical co-deposition of polyaniline and iron oxide nanoparticles from an alkaline medium led to the formation of a novel nanocomposite material with superior adsorption performance for heavy metal ions. By reducing a ferric-triethanolamine complex in the presence of aniline monomers via cyclic voltammetry, a homogenous composite structure can be achieved at room temperature without the need for harsh conditions or additional chemical treatments. The proposed mechanism involves the synergistic combination of the high surface area and magnetic properties of iron oxide with the conductivity and adsorption sites provided by polyaniline. This unique structure enhances the capture efficiency of toxic lead and cadmium ions from aqueous solutions. Therefore, this study introduces a straightforward, eco-friendly electrochemical strategy for fabricating multifunctional nanocomposites targeting efficient heavy metal removal from contaminated water.

2. Experimental

2.1. Materials and chemicals

The materials used were iron(III) chloride hexahydrate, sodium hydroxide, triethanolamine (TEA), aniline monomer, cadmium sulfate, and lead nitrate acquired from commercial sources without added purification except distilling aniline before use. Double distilled water was utilized for all preparations and rinsing steps.

2.2. Electrodes and electrochemical apparatus

A three-electrode electrochemical cell was prepared with a graphite paste working electrode made by compacting graphite powder with paraffin oil binder into a polyester tube. The working electrode was polished before experiments. An Ag/AgCl electrode and platinum foil acted as the reference and counter electrodes respectively. A computerized potentiostat was employed for deposition and testing.

2.3. Synthesis of iron oxide-polyaniline films

The iron oxide-polyaniline composite films were synthesized by cyclic voltammetry electrodeposition from an aqueous solution containing 2 M NaOH, 0.25 M triethanolamine (TEA), 0.12 M FeCl_3 , and 0.3 M aniline monomer. The potential was cycled between +0.425 V and

−1.55 V for 35 cycles at 50 °C, using an optimized scan rate of 0.05 V/s. This process simultaneously induced the oxidation of aniline and the reduction of iron ions, leading to the layered deposition of the composite film onto the cathodic surface.

2.4. Materials characterization techniques

X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) were utilized to determine the structure and composition of the films. Scanning and transmission electron microscopy were employed to examine the structure, respectively. The material's stability was ascertained through the implementation of thermal gradient analysis (TGA). By employing vibrating sample magnetometry (VSM), the magnetic characteristics at room temperature were assessed.

2.5. Adsorption studies

Cadmium and lead ion removal capacity was examined through adsorption isotherm tests using concentration standards from 5 to 100 mg/L prepared from the nitrate and sulfate salts. Metal ion solutions were added to the electrochemical cell and adsorption was carried out under stirred conditions at optimized constant potentials. Residual concentrations were quantified by inductively coupled plasma (ICP) spectroscopy.

3. Results and discussion

3.1. Electrochemical synthesis of PANI/iron oxides nanocomposite

First, the electropolymerization of aniline was optimized in this work. The optimal conditions for the electrochemical synthesis of polyaniline (PANI) were identified as follows: pH = 12.43, scan rate = 50 mV s^{-1} , potential range from +0.90 V to −1.6 V, aniline concentration of 0.3 M, and a temperature of 50 °C. Subsequently, based on the optimized conditions for the electrochemical synthesis of both iron oxides and PANI, the iron oxide-polyaniline (IO/PANI) composite was successfully fabricated.

Fig. 1 illustrates the electrochemical fabrication of the IO/PANI nanocomposite via the cyclic voltammetry technique onto a carbon paste electrode at 50 °C. The electrodeposition bath consisted of 2 M NaOH, 0.25 M triethanolamine (TEA), 0.12 M FeCl_3 , and 0.3 M aniline.

The electrochemical deposition of polyaniline was carried out using a cyclic voltammetry technique. A potential range from +0.425 V to −1.55 V was applied, with a scan rate of 0.05 V/s for 35 cycles. The voltammetric scans were initiated in the positive direction, starting at +0.425 V. This anodic potential facilitates the oxidation of aniline

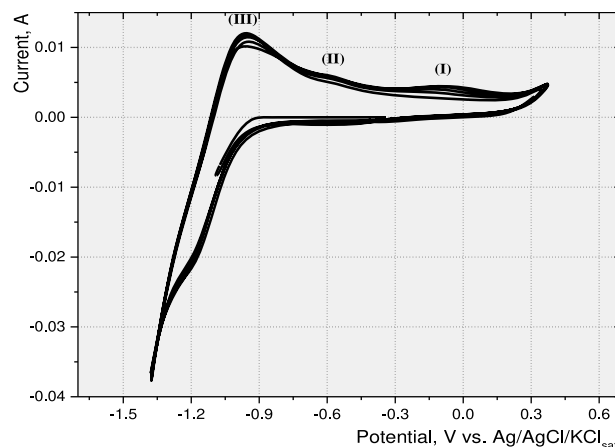


Fig. 1. CV of 0.3 M aniline, 0.12 M FeCl_3 , and 2 M NaOH on CPE for 35 cycles at a ramp rate of 0.050 V/s at 50 °C.

monomers to produce polyaniline deposition on the electrode surface during the first cycle. Controlled potential scanning over multiple cycles leads to a layered buildup of the polyaniline film on the electrode. Key parameters like the potential window, scan rate, and number of cycles can be tuned to optimize the electrodeposition process and polyaniline film properties. After that, the electrodeposition of iron oxides is achieved (second layer), and so on. In our method, the electrosynthesis of this composite was achieved in one step of the used potential range in basic media.

In other reported work [45], PANI/iron oxide composite was electro-synthesized via two potentiostatic successive steps in acidic media. However, in the present work, it is observed that three oxidation peaks appeared at -0.075 , -0.575 , and -0.990 V, respectively, as in Figure 14. The peak (I) should correspond to the oxidation of aniline to form the dimer (p-aminodiphenylamine). At the same time, peak (II) corresponds to the oxidation of a dimer to form polyaniline [25]. These two peaks are shifted to more negative potential compared with the previous work [25]. This shift may be attributed to the presence of electrodeposited iron oxides, which accelerate the polymer formation on its surface. The comparative reduction peak (slight peak), which corresponds to the oxidation peak (II) in this solution (alkaline) is associated with the low protonation degree of p-aminodiphenylamine (ADPA). The third oxidation peak (III) and its comparative reduction peak (at -1.2 V) are attributed to the electrosynthesis of iron oxides [14]. These peaks are confirmed with XRD analysis.

3.2. XRD characterization

X-ray diffraction (XRD) analysis was employed to investigate the phase composition, crystallinity, and structural integration of the electrochemically deposited films. Fig. 2 presents the XRD patterns obtained for the individually synthesized iron oxide, polyaniline (PANI), and iron oxide–PANI (IO/PANI) nanocomposite samples. The electrodeposition process was conducted at 50°C by cyclic voltammetry within a potential window ranging from $+0.425$ V to -1.55 V vs. Ag/AgCl, at a scan rate of 0.05 V s^{-1} for 35 successive cycles. The XRD patterns of the iron oxide sample revealed distinct diffraction peaks corresponding to its crystalline phases, while the PANI sample exhibited characteristic broad peaks indicative of its semi-crystalline nature. In contrast, the IO/PANI composite pattern displayed features corresponding to both components, confirming the successful incorporation of iron oxide nanoparticles within the PANI matrix.

This structural characterization highlights the nature of the interaction between the two phases and verifies the formation of a well-defined nanocomposite through the simultaneous electrochemical oxidation of aniline and reduction of iron ions. The deposition bath used

for the composite synthesis comprised 2 M NaOH as a supporting electrolyte, 0.25 M triethanolamine (TEA) as a complexing agent for iron ions, 0.12 M FeCl_3 as the iron precursor, and 0.3 M aniline as the monomer source. Such detailed XRD analysis provides essential insights into the structural evolution of the electrodeposited layers and the successful formation of a homogeneous composite material with potential applications in electrochemical and adsorption processes.

The same bath composition without aniline was used for the electrochemical synthesis of iron oxides. For the electrodeposition of PANI, the same bath without the ferric salt was utilized. It can be observed that there are six peaks at 2θ of 21.90° , 25.10° , 28.05° , 31.1° , 36.23° , and 54.1° , which are similar to those of the standard PANI-HCl salt (semi-crystalline nature). These peaks are similar to those reported in the literature [46]. At the same time, these peaks didn't appear at the XRD patterns of iron oxides (c), which emphasized that these peaks are for PANI. The intensity of peaks at $2\theta = 25.1^\circ$ and 54.1° is diminished at the XRD pattern of composite (b) due to the interaction between PANI and iron oxides. However, the XRD pattern of iron oxides/PANI has not only the two broad peaks of PANI, which are located at $2\theta = 21.90^\circ$ and 54.1° , but all the sharp peaks of iron oxides are observed. The XRD analysis provides evidence that iron oxides were successfully incorporated into the polyaniline matrix in the composite film. Specifically, new peaks are observed at 2θ values of 25.1° and 28.05° in the iron oxide/PANI pattern. These peaks correspond to the repeating periodicity along the parallel and perpendicular orientations relative to the PANI polymer chains. Their presence confirms the iron oxide nanoparticles were integrated into the ordered structure of the conductive polyaniline chains during the synthesis of the composite. This structural characterization demonstrates the electrodeposition method can be used to deposit hybrid iron oxide-conducting polymer thin films [46]. There is a peak at $2\theta = 58.52^\circ$ appeared only in the XRD pattern of iron oxides/PANI, which is the characteristic peak of the composite. The sharp peaks reveal that iron oxides/PANI and PANI are polycrystalline.

3.3. FTIR spectroscopy

Fourier transform infrared spectroscopy (FTIR) was employed to investigate the chemical structure and functional group interactions within the electrodeposited polyaniline (PANI) and iron oxide–polyaniline (IO/PANI) composite films. Fig. 3 displays the FTIR spectra recorded for the electrochemically synthesized PANI and IO/PANI samples deposited onto copper substrates. The FTIR spectrum of the IO/PANI composite shows the characteristic vibrational bands associated with PANI, including the N–H stretching vibration at 3285 cm^{-1} , the C = C stretching mode of the quinoid ring at 1430 cm^{-1} , the C–C stretching vibration of the benzenoid ring at 1389 cm^{-1} , and the out-

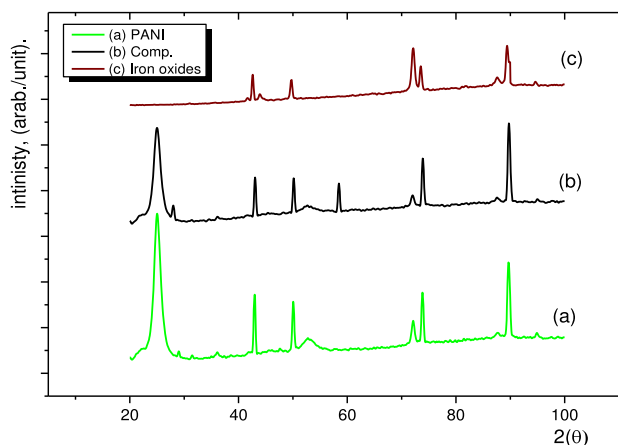


Fig. 2. XRD patterns of the electrochemically deposited (a) PANI, (b) Iron oxides-PANI nanocomposite, and (c) iron oxide nanoparticles.

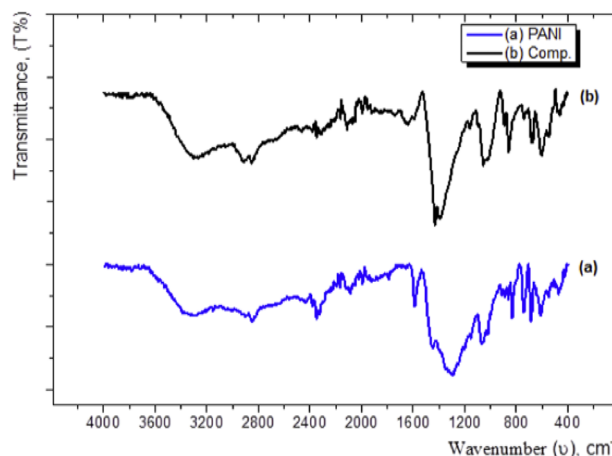


Fig. 3. FTIR spectra for PANI and iron oxides/PANI were recorded at the spectral range $400\text{--}4000\text{ cm}^{-1}$.