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Determination of 2-Nitrophenol by Electrochemical Synthesized Mg/Fe Layered Double Hydroxide Sensor

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A novel, cheap and simple non-enzymatic amperometric sensor was fabricated based on electrodeposition of Mg/Fe layered double hydroxides (Mg/Fe-LDH) on glassy carbon (GC) electrode. The electrochemical synthesized Mg/Fe-LDH was characterized by the scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) and cyclic voltammetry (CV) methods. The prepared Mg/Fe-LDH was found to have an excellent electrocatalytic activity toward the reduction of 2-Nitrophenol (2-NP). It has been shown that the Mg/Fe-LDH modified electrode, can be used as non-enzymatic amperometric sensor for determination of 2-NP in concentration range of 5-560μM with limit of detection of 4μM. The proposed method was used for determination of 2-nitrophenol in industrial waste waters. In addition, the modified electrode with Mg/Fe-LDH exhibited satisfactory reproducibility and a long-time stability.

Keywords: Electrochemical synthesis, Layered double hydroxide, 2-Nitrophenol, Amperometric sensor

1. INTRODUCTION

Layered double hydroxides (LDHs) are known as anionic clays and can be described by the generic formula $[M_{1-x}^{2+} M_x^{3+} (OH)_2]^{x+}[A_{x/n}]^{n-}\cdot mH_2O$ where M^{2+} represents any divalent metal cation (Mg^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+} ,etc), M^{3+}any trivalent metal cation (Al, Ga, Cr, Fe, etc) , x is equal to the molar ratio of $M^{2+}/(M^{2+}M^{3+})$ in the range 0.2–0.33 and A^{n-} an anion (inorganic or organic) [1-3].

The LDH consists of $M^{II}(OH)_6$ and $M^{III}(OH)_6$ edge-sharing octahedral forming sheets similar to those of brucite [4] . Single crystal XRD analysis, shows that all the cations are placed in the same layer and the positive charge of layers is balanced by intercalation of anions (Cl^-, NO_3^-, CO_3^{2-}, SO_4^{2-} and, usually, water molecules) located in the interlayer region [5,6]. Therefore, LDH presents a lamellar structure and intercalation properties similar to that of cationic clays, but with a higher charge density of the layers (anionic exchange capacity~2 mequiv g^{-1}) [4]. In recent years, LDHs, have attracted growing interest for using in the wide fields owing to their good biocompatibility [7], large surface area (100±300 m^2/g) [8], high anion exchange capacity[9], intense adsorbability [10], high catalytic activity [11], Memory effect, which allows reconstruction under mild conditions (after calcination until 500 °C) of the original structure by contact with solutions containing various anions and good thermal and chemical stability [2,5]. LDHs have potential application in a wide range of important areas, i.e. medicine [2], catalysis [12], electrochemistry (as biosensors based on clay-modified electrodes), anion exchangers, photochemistry[13], adsorbents [14], electro- and photoactive materials[15], solid-state nanoreactors [16,17].

Nitrophenols are a family of nitrated phenols, being important chemicals, with wide usage in the petroleum, gas, wood, textile, pharmaceutical, paper-making, insecticide, and dyestuff industries. The determination of nitrophenol (NP) compounds in environmental samples has been well attended because they have toxic effects on environment, human, animals, and plants. Therefore, the determination of nitrophenol isomers is an important environmental analysis. There are some analytical methods such as flow-injection analysis, spectrophotometry, high-performance liquid chromatography, and capillary electrophoresis for this purpose [18-20]. Electrochemical methods have also been applied for determination of the NP isomers [21,22]. The methods, such as differential pulse polarography (DPP) and differential pulse voltammetry (DPV) offer high sensitivity, low limit of determination, easy operation, and simple instrumentation. DPP was also employed for the determination of trace amounts nitrobenzene [21,23]. But the greatest drawback of polarography and mercury film electrodes is toxicity of mercury and the mercury salts employed for the preparation of mercury electrodes. Thus, electrode materials are always being sought to replace mercury[24].

Chemical methods are used mainly for preparing LDHs. Usually chemical synthesis has disadvantages including prolonged synthesis time, while the electrochemical synthesis is very fast, comfortable and has high purity. In the present work, Mg/Fe-LDH was synthesized simply via electrodeposition method on glassy carbon electrode and its voltammetric behavior was investigated. The formation of LDH was confirmed by the FT-IR, XRD, EDAX and cyclic voltammetry methods. Then the LDH-modified electrode was used for the electrocatalytic reduction and determination of 2-Nitrophenol(2-NP).

2. EXPERIMENTAL

2.1 Apparatus and software

All electrochemical experiments were performed with Sama500 Electrochemical Analysis System (Esfahan, Iran) interfaced with a personal computer. A three-electrode cell, containing a modified glassy carbon electrode (2mm in diameter) with Mg/Fe-LDH as working electrode, a

Saturated Calomel Electrode (SCE) as reference electrode and a platinum wire auxiliary electrode, were used. All the potentials in the text refer to SCE. The pH measurements were carried out by means of Metrohm pH-Meter 691. The X-ray diffraction (XRD) patterns were recorded with a Bruker AXS model D8 Advance diffractometer using Cu-K_α radiation ($\lambda = 1.542$ Å), with the Bragg angle of 6–70° and performing steps of 0.04° (2Θ) counting 4 s/step. The Scanning Electron Microscopy (SEM)/Energy Dispersive X-ray analysis (EDAX) analysis was performed using a Hitachi S4160 Scanning Electron Microscope equipped with an EDAX system. The accelerating voltage was 10 kV with the beam current of 1 nA and the spectra collection time of 100 s. The FT-IR spectra was obtained using KBr disk method at room temperature with a Shimadzu 8400s spectrophotometer in the range of 4000– 400 cm^{-1}.

2.2 Reagents and standard solutions

All reagents were of analytical grade. The water utilized in all studies was double distilled and deionized. Stock solution of 2-NP (10^{-3} M) was prepared by weighing suitable amounts of this compound and dissolving it in water. This solution was diluted up to the required concentrations using the same solvent. Britton–Robinson (B–R) buffer (0.1M) was prepared by dissolving appropriate amounts of boric acid, orthophosphoric acid and glacial acetic acid in water and adjusting to the desired pH value using sodium hydroxide. The real samples were obtained from the Shahid Salimi industrial zone (Tabriz, Iran), and Urmia ShahrChaee River (Urmia, Iran).

2.3 Preparation of 2-NP solutions

The general procedure for obtaining voltammograms was as follows. An appropriate amount of standard 2-NP solution was added into a 10-mL volumetric flask, 2.0 mL of Britton–Robinson buffer solution and then the solutions were diluted to the mark with distilled water. After 5 s, the voltammograms were recorded by applying a negative going scan over the potential range from -0.2 to -1.4V. The obtained voltammograms were used for further calculations. All measurements were made at 25°C.

2.4 Fabrication of the modified Mg/Fe-LDH electrode

First, the bare glassy carbon electrode was polished with alumina powder of 0.05 μM diameter on a wet polishing cloth. After each polishing, the electrode was sonicated in doubly distilled water for 10 min in order to remove any adsorbed substances. Finally, it was dried with acetone.

A thin film of Mg/Fe-LDH was electrochemically deposited on the cleaned GC electrode at optimum conditions: applying constant potential of −0.9 V for 60s in an aqueous solution containing $Mg(NO_3)_2$ 0.12M, $Fe(NO_3)_3$ 0.04M and KNO_3 0.15M. The following reactions, on the electrode surface, may be acting in the preparation of modified electrode:

$$NO_3^- + H_2O + 2e^- \longrightarrow NO_2^- + 2OH^- \tag{1}$$

$$Fe^{3+} + e \rightarrow Fe^{2+} \qquad (2)$$

$$(1-x-y)Mg^{2+} + yFe^{2+} + xFe^{3+} + 2OH^{-} + xNO_3^{-} + mH_2O \longrightarrow [Mg^{2+}_{(1-x-y)}Fe^{2+}_{y}Fe^{3+}_{x}(OH)_2]^{x+}NO^{-}_{3x}.mH_2O$$

Assuming that the formula of the Mg/Fe-LDH was expressed to be [25,26]:

$$[Mg^{2+}_{(1-x-y)}Fe^{2+}_{y}Fe^{3+}_{x}(OH)_2]^{x+}NO^{-}_{3\;x}.mH_2O$$

after modification, the electrode was thoroughly rinsed with water and kept at room temperature for further use.

3. RESULTS AND DISCUSSION

3.1 Characterization of the modified Mg/Fe-LDH

SEM was employed to explore the morphology of the prepared Mg/Fe-LDH. The SEM micrograph in Fig. 1A shows the morphology of the LDH film on glassy carbon electrode.

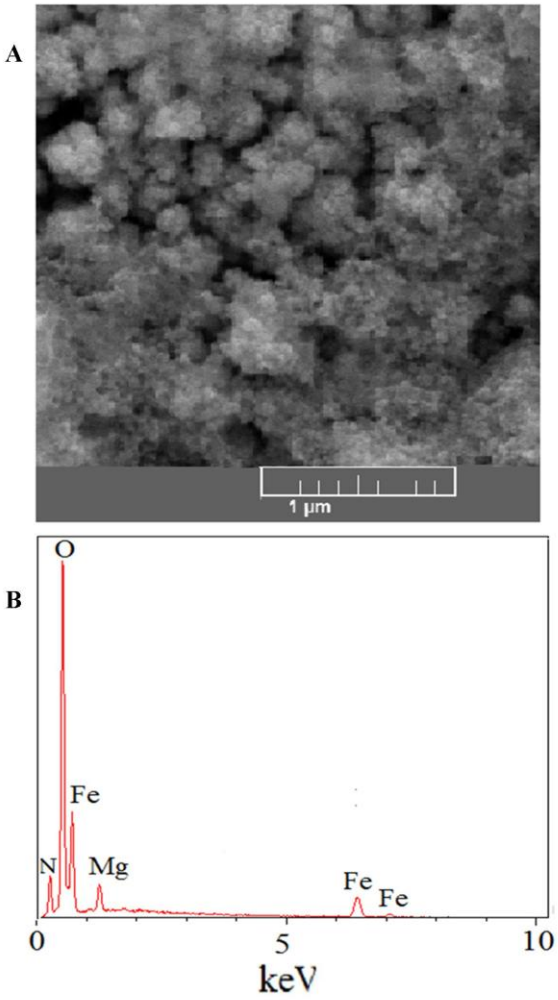

Figure 1. (A) ~~FE~~SEM image of the Mg/Fe-LDH electrosynthesized from a solution with a Mg/Fe ratio of 3/1(Mg^{2+}0.12M and Fe^{3+} 0.04M) for 60s deposition time, (B) EDAX result of the Mg/Fe–LDH

As it is clear from Fig. 1A, the sample consisted of pseudo-spherical particles when observed using the SEM and the LDH particles with size below 100 nm are shown in Figure. The EDAX analysis was also performed on the same film to study the elemental composition of the deposited material on the electrode surface. From Fig. 1B it can be observed that Mg and Fe elements composed of Mg/Fe-LDH were present on the electrode surface.

The FT-IR spectrum of Mg/Fe-LDH thin film at room temperature is shown in Figure. 2 confirming the formation of the Mg/Fe-LDH phase. The broad and intense band centered at 3400 cm^{-1} is due to the -O–H stretching vibrations of the layer hydroxides on the surface and intercalated water molecules [27] which are observed at lower frequency in the LDH instead of the O-H stretching vibration in normal liquid water.

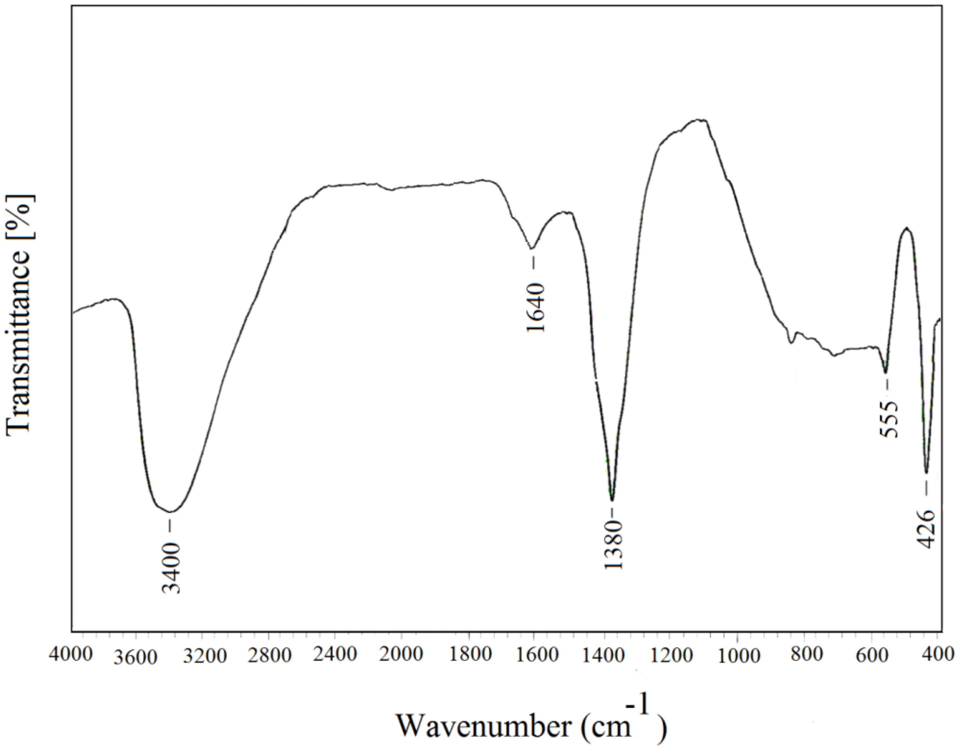

Figure 2. FT-IR spectrum of the Mg/Fe-layered double hydroxide electrosynthesized from a solution with a Mg/Fe ratio of 3/1 for 60 s deposition time.

This indicates that water is present in the LDH interlayers, where it has some sort of hydrogen bond type interaction with other anions as well as with hydroxide groups of layers [28]. Absorption at 1380 cm^{-1} is related to the υ_3 vibration of NO_3^- [29]. Also, a band of medium intensity at 1640 cm^{-1} is due to the bending mode of water molecules [30]. Below 1000 cm^{-1}, the bands corresponding to the stretching modes of the brucite-like layers, are present. The bands centered at 555 and 426 cm^{-1} are attributed to M-O-H and O-M-O lattice vibrations [27, 29].

Figure 3 shows the XRD patterns of the as-prepared Mg/Fe-LDH thin film in the range of 2θ = 6–70° showing a low crystallinity due to the low amount of the LDH material on the electrode surface and probably the fast kinetics of the LDH precipitation which hinders an ordered stacking of the brucite layers.

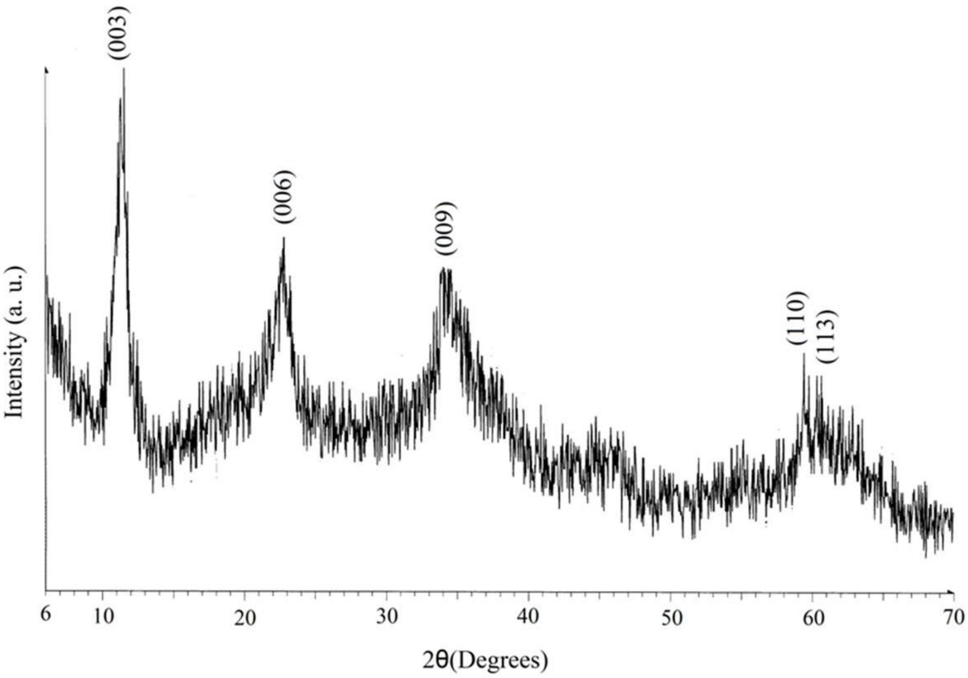

Figure 3. The XRD patterns for Mg/Fe-LDH.

The patterns in Fig. 3 fit well to layered double hydroxide with basal reflections of hkl planes (003), (006), (009), (110) and (113)[31-33]. No reflections of impurities were observed, which indicates high purity of the product. The (003) reflection located on the 2θ angle of ~11.26° is typical of hydrotalcite-type materials [34,35], that indicates a basal spacing of ~0.78 nm, quite similar to those at earlier [30] and is compatible with that in a nitrate containing LDH structure [27]. The $2\theta = 60^{o}$ line is also a characteristic of the hydrotalcite structure.

3.2 Electrochemical behavior of the modified electrode

The effects of deposition potential, deposition time and Mg/Fe ratio were investigated in the fabrication modified electrode step. The deposition potentials were changed from −0.6 to −1.2V. For the deposition process, potentials more positive than −0.9 V are not favorable and the LDH is not formed in this case. Also, the Mg/Fe-LDH exhibits a decreased activity at the potentials more negative than −0.9 V. A very important feature of the voltammetric curves is the fact that anodic and cathodic peak currents increases and ΔE_p decreases with increasing of the deposition time until the deposition time reaches 60s. After 60s ΔE_p also increases with increasing of the deposition time. The increase of the peak heights can be easily explained by the increase of Fe(II)/Fe(III) sites. The same investigations were done for Mg/Fe ratio and the optimum Mg/Fe ratio for the electrochemical synthesis was found to be 3:1.

The influence of scan rate on the peak potential was investigated by cyclic voltammetry. Figure 4 shows the cyclic voltammograms of Mg/Fe-LDH modified GCE electrode in 0.1 M NaOH (pH=13) solution at different scan rate (from 50 to 240 mVs^{-1}). A pair of well-defined redox peaks was observed at the Mg/Fe-LDH electrode, which is assigned to the Fe(II)-LDH/Fe(III)-LDH redox. These peaks confirm the presence of Fe(II) and Fe(III) in LDH. The dependence of cathodic peak currents to the scan rate is shown as inset in Fig. 4. As shown in inset of Fig. 4, the cathodic peak currents increase linearly with the increase of the scan rates, indicating a thin layer-like behavior.

The effect of the pH on the electrochemical behavior of the modified electrode was investigated by the cyclic voltammetry at the scan rate of 100mVs^{-1}. The pH of the solutions was changed using buffer solutions ranging from pH 5 to 13 (see Fig.5). At the pHs less than 9 there was not any peaks for the modified electrodes. On the other hand, the intensity of peaks increases at pH > 9. At the pH 13, redox peaks of Fe(III)-LDH/Fe(II)-LDH were the highest and ΔE_p was minimum.

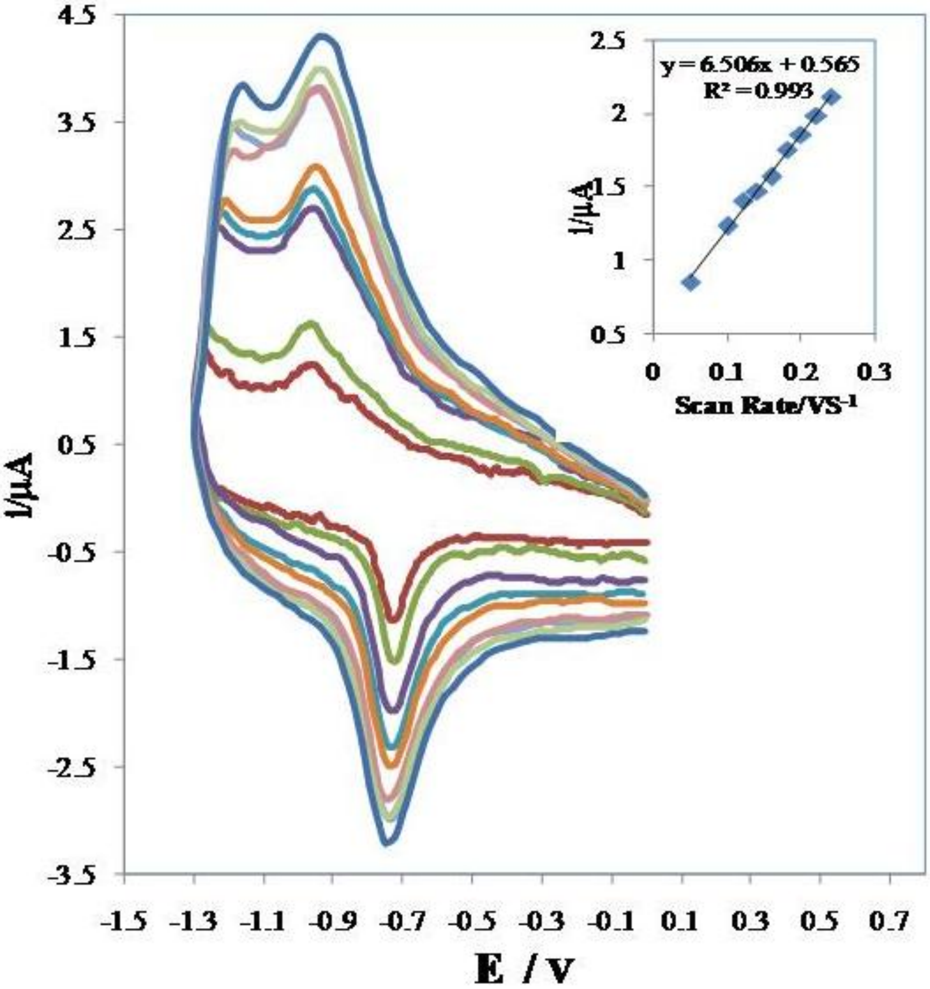

Figure 4. Cyclic voltammograms of Mg/Fe-LDH in pH 13 at different scan rates. The scan rates are (a-i) 50 to 240 mVs^{-1}, respectively. Inset: The linear dependence of anodic and cathodic peak currents vs. scan rate.

The best signals relevant to the couple Fe(III)/Fe(II) are observable in the pH 13 and can be described by the following reaction:

$Fe(III)(OH^{-})\text{-}LDH + e \leftrightarrows Fe(II)\text{-}LDH + OH^{-}_{(sol)}$

From these results, pH 13 was selected for further studies.

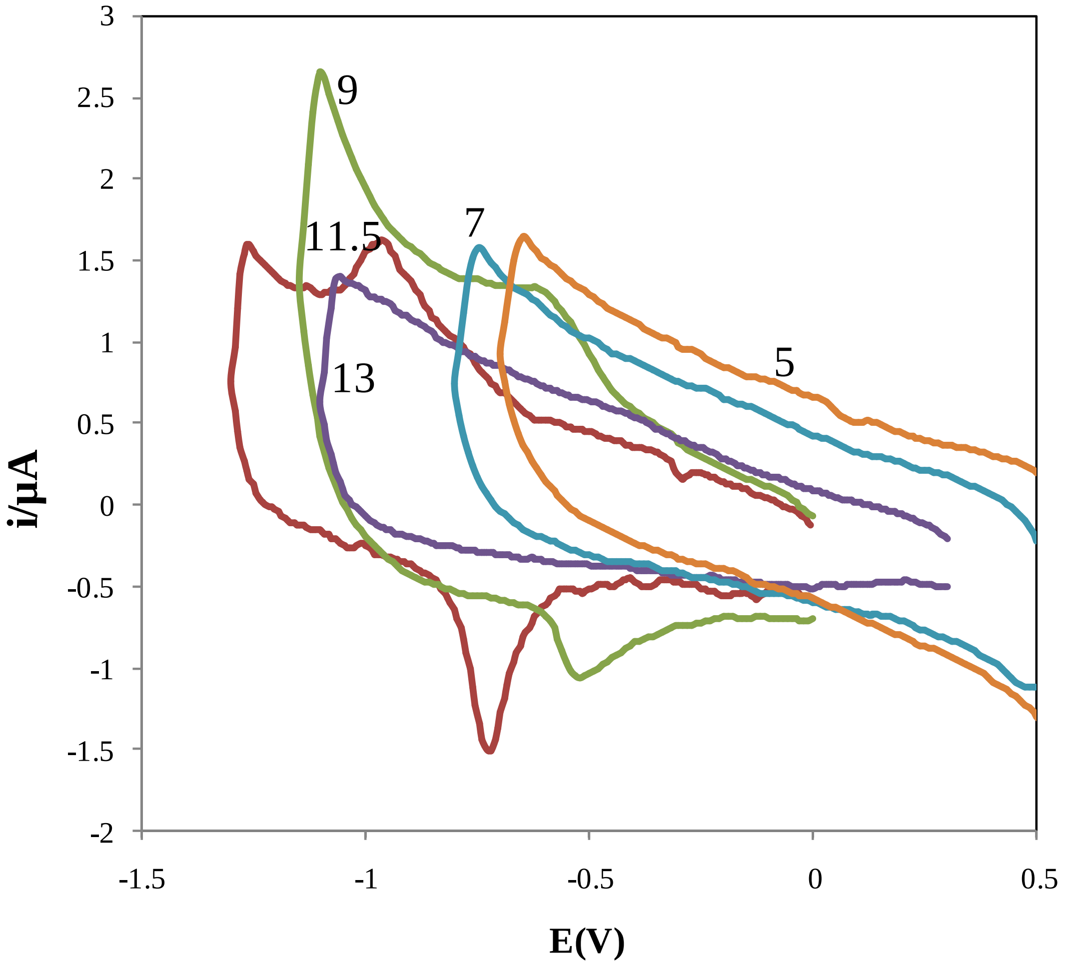

Figure 5. Cyclic voltammograms recorded for Mg /Fe-LDH in pH 5–13 at the scan rate of $100 mVs^{-1}$.

3.4. Electrocatalytic behavior of Mg/Fe-LDH toward electroreduction of 2-Nitrophenol

Figure 6 shows the typical cyclic voltammograms of 0.340mM 2-NP on the bare glassy carbon electrode (a) and Mg/Fe-LDH modified glassy carbon electrode at pH 13 solution (b). The voltammograms of (c) shows the background. At the bare glassy carbon electrode the reduction peak potential of 2-Nitrophenol was located at -110mV. On the Mg/Fe-LDH modified glassy carbon the reduction peak current of 2-NP were increased to about 2 times that of bare glassy carbon electrode. Also a positive shift of Ep was observed with the Ep value decreased to -900 mV. Comparing the data at the bare and modified electrode, the electrocatalytic reduction of 2-NP on Mg/Fe-LDH modified glassy carbon electrode was confirmed.

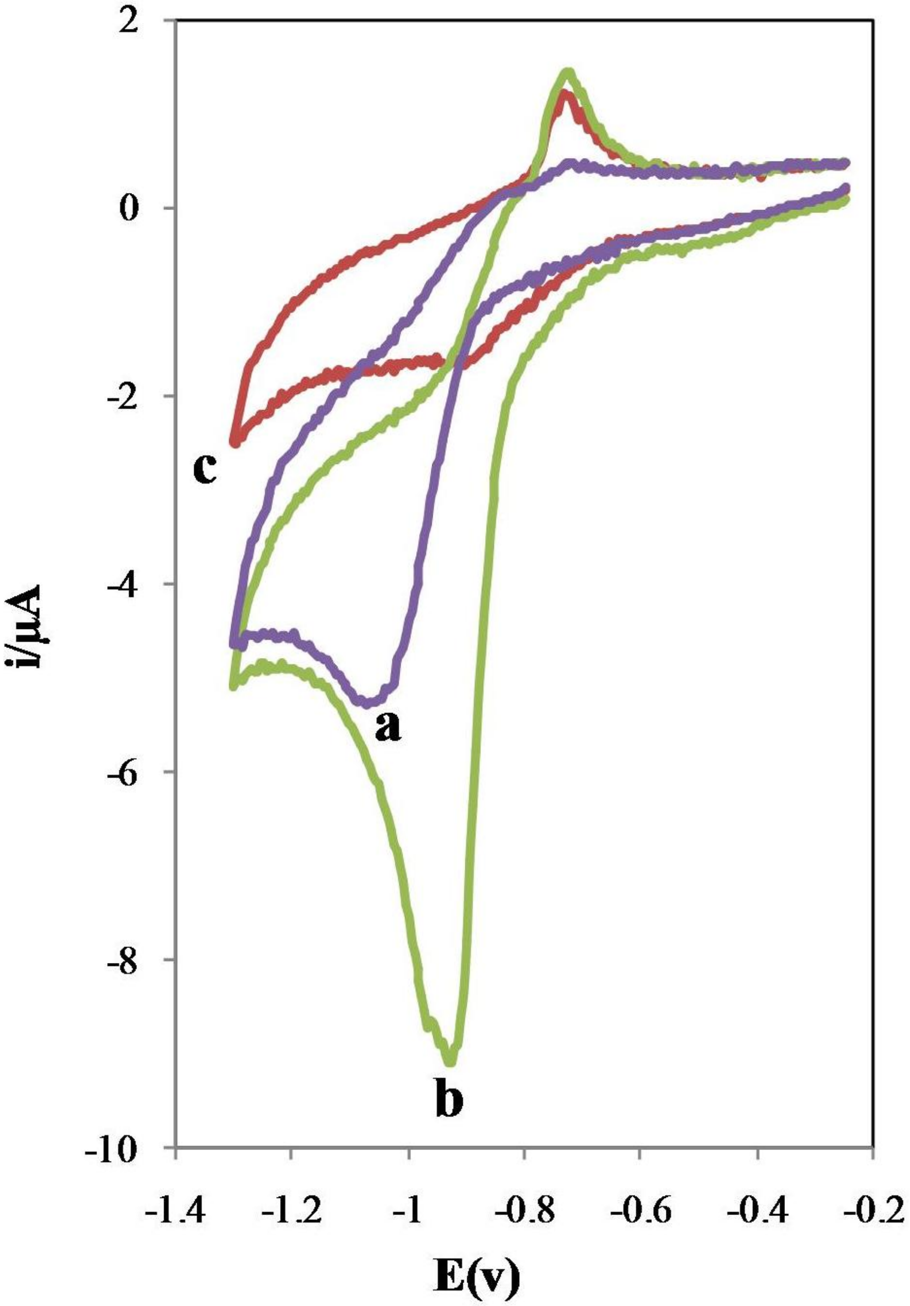

Figure 6. Cyclic voltammograms of 0.34 mM 2-NP at a bare (a) and Mg/Fe-LDH modified (b) glassy carbon electrode in pH 13 solution. The voltammogram of (c) is the background.

Figure 7 shows the CVs of Mg/Fe-LDH modified glassy carbon electrode in 0.1 M NaOH solution containing 0.34 mM 2-NP at different scan rates from 50 to 240mVs^{-1}. The dependence of peak current to the scan rate has been explored and the corresponding plot is shown as inset in Fig. 7. On the Mg/Fe-LDH electrode the cathodic peak currents vary linearly with the square root of scan rate ($\nu^{1/2}$) in the range of 50–240 mVs$^{–1}$, signifying the dominance of a diffusion process as the rate limiting step.

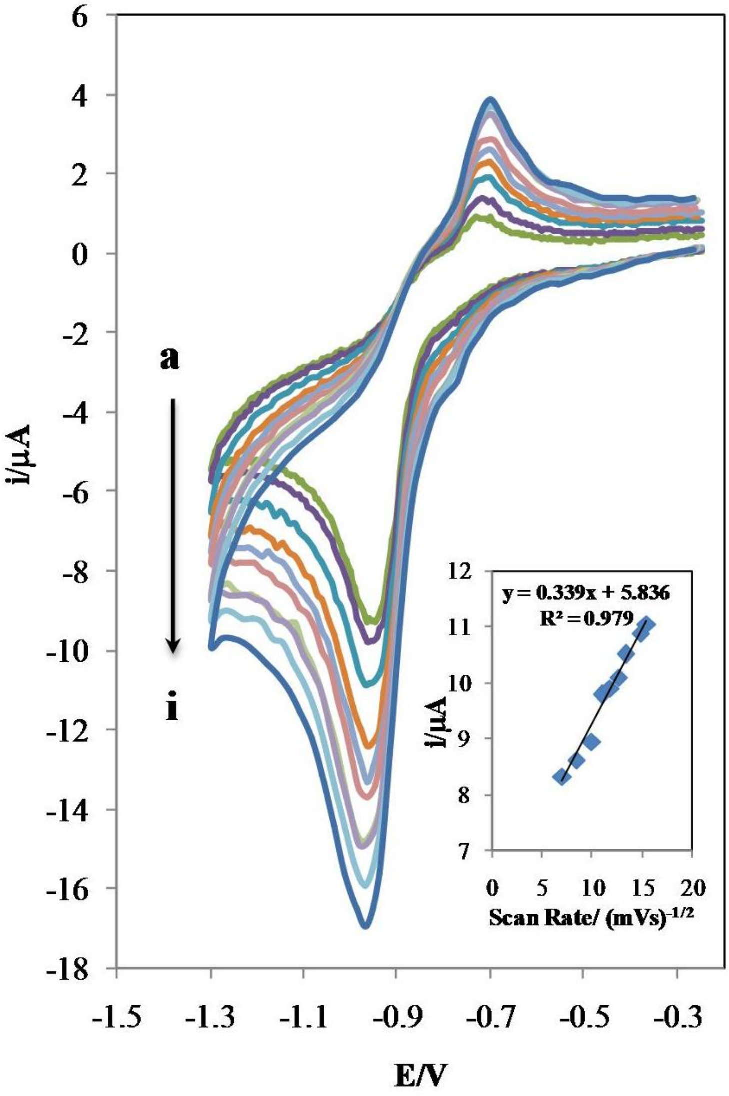

Figure 7. Cyclic voltammorams of Mg/Fe-LDH in pH 13 containing 34 mM 2-NP at different scan rates from 50 to 240mVs^{-1}. Inset: Dependence of the peak current with square root of the scan rate.

The following mechanism may be proposed for the reduction of 2-NP on the Mg/Fe-LDH-modified electrode:

4Fe(III)-LDH → 4 Fe(II)-LDH+4e (Electrochemically)
R-NO_2 + 4Fe(II)-LDH +4 H_2O → R-NHOH + 4 Fe(III)-LDH + $4OH^-$ (Chemically)

Figure 8 shows the typical amperometric response of the prepared LDH modified electrode to 2-NP with the successive addition of 2-NP into continuously stirred 0.1M NaOH. The applied potential was -1.1 V. The amperometric sensor exhibited rapid and sensitive response to the change of 2-NP concentration and an obvious increase in the reduction current upon successive addition of 2-NP were obtained. The inset in Fig. 8 shows the corresponding calibration curve of the prepared amperometric

2-NP sensor. The response of the Mg/Fe-LDH prepared modified electrode increased linearly over the 2-NP concentration range from 5μM to 640μM with a sensitivity of 218.4μAmM^{-1}, and the detection limit of 4μM.

The stability and reproducibility of the Mg/Fe-LDH fabrication was evaluated via the comparison of the sensitivity and peak currents of different electrodes for same samples. Five different Mg/Fe-LDH modified electrodes were prepared independently and were used for cyclic voltammetry and amperometric determination of 2-NP at pH 13. The R.S.D. for i_p and E_p of voltammograms was less than 5% and RSD value for sensitivities was 5.2%. The stability of the Mg/Fe-LDH modified electrodes, stored at room temperature, was investigated by the cyclic voltammetry. After two weeks, their cyclic voltammograms were recorded at pH 13, and the R.S.D. for ip and Ep of voltammograms was found to be less than 6%.

In order to show the reliability of the modified electrode, the proposed method was applied to determination of 2-NP in real samples. The real samples were taken from the Shahid Salimi industrial zone (Tabriz, Iran) and Urmia ShahrChaee River (Urmia, Iran) waters. In these samples there were no peaks. In other words, there was not 2-nitrophol at the samples. Therefore, we used the spiking method to show the reliability of the proposed method. The same results were obtained when the real samples were analysised with liquid–liquid extraction/gas chromatography (GC) as a standard method [36].

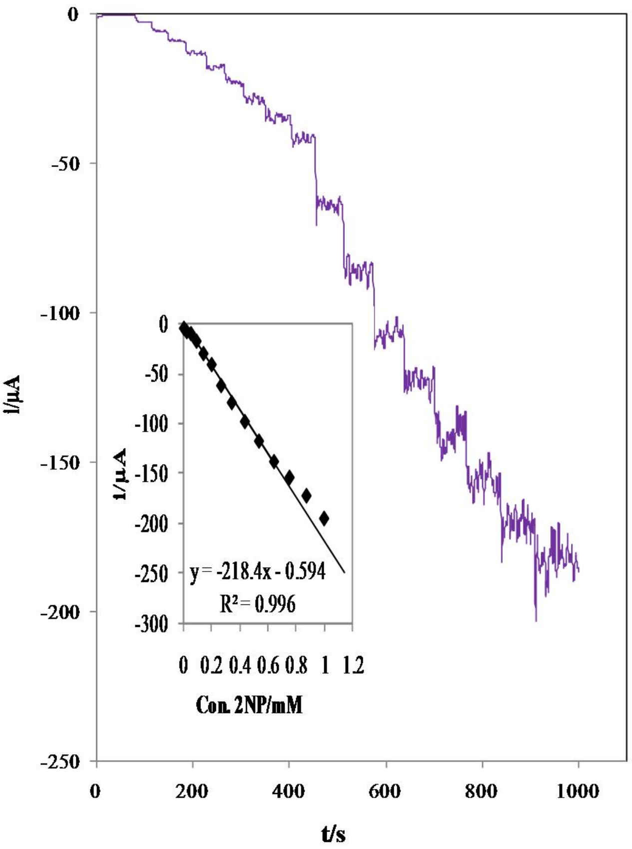

Figure 8. Amperometric response of Mg/Fe-LDH modified glassy carbon electrode kept in −1.10 V in 0.1 M NaOH solution containing different concentrations of 2NPfrom 5.0 to 640μM. Insets: calibration plot of 2-NP by amperometry technique.

Table1 summarizes the results obtained for real samples. Table 1 also shows that satisfactory recovery values were obtained for these samples.

Table 1. Results applied on the spiked in industrial waste water and river samples (10^{-6}M)

Sample	Added	Found	Recovery(%)
Industrial waste water	49.5	47.1	95.1
	49.5	48.4	97.8
	49.5	49.6	100.2
Urmia ShahrChaee River water	75.5	74.7	98.9
	75.5	75.9	100.5
	75.5	74.6	98.8

4. CONCLUSION

In this work, Mg/Fe layered double hydroxide was electrochemically synthesized on the glassy carbon electrode. The LDH film has been prepared by reduction in potentiostatic conditions of Mg^{2+} and Fe^{3+} nitrates solution. Based on experimental results, we have hypothesized that the $Mg^{2+}/Fe^{2+}/Fe^{3+}$ LDH was formed on the GC electrode. The control of the film composition and thickness is possible by this synthetic approach. The synthesis process is simple, quick and reproducibility of the LDH synthesis is very good.

The Mg/Fe-LDH modified glassy carbon electrode exhibited high sensitivity, long-time stability, a wide range and low the limit of detection for electrocatalytic detecting 2-Nitrophenol. The Mg/Fe-LDH modified GC electrode has been applied to the determination of 2-Nitrophenol in real samples.

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