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Two-step fabrication of iron-containing polyaniline composites for electrocatalytic hydrogenation of nitroarenes

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ABSTRACT

Polyaniline + Fe + FeO + Fe_3O_4 composites were prepared as powder by a two-step process: (1) introduction of FeO into oxidative polymerization of aniline and (2) electrochemical reduction of the powder deposited on a Cu cathode in aqueous NaOH. The structure and morphological features were studied by atomic emission spectroscopy, X-ray diffraction analysis and electron microscopy. The polyaniline–iron composites were used in electrohydrogenation of *p*-nitrobenzoic acid (*p*-NBA). Their electrocatalytic activity in the process is due to the formation of iron particles as a result of the electrochemical reduction of Fe^{2+} cations in FeO. The electrocatalytic activity is clearly demonstrated by the electrocatalytic hydrogenolysis of the intermediate hydroxylaminobenzoate to the aminobenzoate. Magnetic properties have been determined for the composite with optimal FeO content before and after the electrocatalytic hydrogenation of *p*-NBA.

1. Introduction

The introduction of metal-containing inorganic compounds in the form of oxides, hydroxides, metal salts and their nanoparticles into polymer matrices makes it possible to obtain new composite materials possessing specific physicochemical properties (optical, electrically conductive, magnetic, catalytic, etc.) [1,2]. Polyaniline (PAni) is one of the most promising electrically conductive polymers due to the simplicity of preparation, low cost of the initial monomer and the ability to change its physicochemical properties depending on the acidity of the medium, the degree of oxidation of the polymer backbone and the particle morphology [3]. Close attention is paid to iron-containing PAni composites due to the possibility of creating materials with unique magnetic and conductive properties [1,4–13]. The usual subjects of research are metal–polymer composites with Fe_3O_4 and Fe_2O_3 iron oxides.

In our studies of polyaniline–metal composites [14,15], it was established that the introduction of the metal salt into the polymer by chemical methods followed by the use of the resulting composites to activate a cathode in the electrochemical reduction of organic compounds is accompanied by the formation of metal particles in the zero-valence state. However, cathodic activation by PAni composites with the introduced iron (II, III) salt does not lead to the reduction of its cations, and the formation of composites with Fe^0-particles.

In this work, PAni + Fe^0 + FeO + Fe_3O_4 composites were prepared by incorporating the FeO (wüstite) powder sonicated into oxidative polymerization of aniline and subsequent reduction in an electrochemical cell. The electrocatalytic activity of the resulting iron-containing composites toward the electrocatalytic hydrogenation of *p*-nitrobenzoic acid (*p*-NBA) has been studied. The hydrogenation product, *p*-aminobenzoic acid, is of great practical importance, as it belongs to the vitamins of group B and is a precursor in the synthesis of folic acid, as well as participating in various other organic syntheses. It should be noted that iron-containing composites without PAni (Fe + FeO + Fe_3O_4), according to [16], exhibit stable and high electrochemical characteristics when used as an anode material in lithium-ion batteries.

2. Experimental

Iron-containing PAni composites were obtained by introducing the FeO iron oxide into the reaction medium of oxidative polymerization of aniline (ammonium persulfate was used as an oxidizer). The ratios of aniline/FeO were 1:0.2, 1:0.4, 1:0.6, 1:0.8, 1:1 and 1:1.5. The iron oxide was pre-treated with ultrasound in distilled water for 20 min. It was then introduced into the reaction mixture after its pH had been raised to 8 by an addition of 1 M NH_4OH solution. The resulting mixture was left for 24 h. The precipitate was filtered off and washed with

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Table 1
Electrocatalytic hydrogenation of *p*-NBA on PAni + FeO composites.

Entry	Composites	Iron content in 1 g of composite, g	*W*, mL H_2/min (α = 0.25)	*η*, % (α = 0.25)	*α*, %	$Q_I + Q_{II}$, A·min	Current efficiency for stage II, %
1	Cu cathode	–	3.7	34.6	70.1	30 + 225	13.92
2	Pb cathode	–	6.2	60.3	80.2	75 + 127	28.21
3	PAni + FeO (1:0,2)	0.134	4.6	41.4	67.4	45 + 135	22.30
4	PAni + FeO (1:0,4)	0.284	4.3	38.0	73.1	45 + 165	19.79
5	PAni + FeO (1:0,6)	0.291	6.4	47.0	96.0	45 + 135	31.76
6	PAni + FeO (1:0,8)	0.326	5.6	54.2	82.8	60 + 150	24.66
7	PAni + FeO (1:1)	0.410	6.0	52.2	87.4	52 + 150	26.03
8	PAni + FeO (1:1) - 2 (Cu)	0.404	7.2	70.8	92.7	60 + 150	27.61
9	PAni + FeO (1:1) - 2 (Pb)	0.404	7.7	77.5	83.6	75 + 135	27.66
10	PAni + FeO (1:1,5)	0.486	3.6	30.4	90.3	30 + 165	24.45

distilled water, then with acetone, and dried at 80 °C. The PAni + FeO (1:1) - 2 composite was re-synthesized later for a comparison of the results of the electrohydrogenation of *p*-NBA on the Cu and Pb cathodes. Some disagreements with the previously obtained results for Pani + FeO (1:1) composite deposited on a Cu cathode (see the data in Table 1 below) are caused by difficulties in reproducing in the synthesis of these composites all the fine details of the structure of the polymer matrix (polyaniline) and the distribution of dopant particles therein, which affect the properties of the composites.

The iron content (Fe^{2+} and Fe^{3+}) in the filtrates after the synthesis of PAni composites was determined by atomic emission spectroscopy; the iron content in the resulting powdered composites was then calculated using the difference with the initial metal content in the FeO.

The structure and phase constitution of the synthesized PAni + FeO composites were studied by X-ray diffraction (XRD) analysis on DRON-2 diffractometer. Their morphological features were investigated using a TESCAN MIRA 3 LMU scanning electron microscope.

Experiments on the electrocatalytic hydrogenation of *p*-nitrobenzoic acid were carried out in a diaphragm electrochemical cell with an external magnet under the cathode, as described in [14,15]. The iron-oxides-containing PAni composite (weighing 1 g) was deposited on a horizontally placed copper cathode and for comparison on a lead cathode. The current density was 1.19 kA/m^2 (I = 1.5 A, the area of the visible cathode surface is 0.126 dm^2), the temperature 30 °C. The 75 mL of 2% NaOH solution was used as a catholyte (an anolyte – 60 mL of 20% NaOH solution). At first, the PAni + FeO composites were saturated with hydrogen, until the ratio of gases evolved $V(H_2):V(O_2) = 2:1$ was established. Then, the organic compound (0.774 g of *p*-NBA) was injected into the cell. The average rate of the hydrogenation reaction (*W*), hydrogen utilization coefficient (*η*) and conversion of *p*-NBA (*α*) were calculated by the following relations: $W = \Delta V_t / \Delta t$ (the average rate was determined from these data up to α = 25%); $\eta = [(2\,V(O_2) - V(H_2)] / 2\,V(O_2)] \cdot 100\%$ at the value of $\alpha = 25\%$, and $\alpha = V_t / V_{theor.} \cdot 100\%$, where V_t is a volume of absorbed hydrogen at the reaction time *t* determined using the volumes of gases evolved $V_t = k(2\,V(O_2) - V(H_2))$ (*k* is a barometric coefficient); $V_{theor.}$ is the calculated volume of hydrogen for complete hydrogenation of the nitro group in the starting amount of *p*-NBA.

The magnetic characteristics of PAni composite with an aniline/FeO ratio of 1:0.6 before (*1*) and after (*2*) electrocatalytic hydrogenation of *p*-NBA were determined by the vibration method on the automated system Cryogenic VSM CFS-9T-CVTI. The measurements were performed at a temperature of 300 K in the magnetic field range up to 40 kOe.

3. Results and discussion

Oxidative polymerization of aniline in a hydrochloric acid medium using ammonium persulfate was discussed in detail in [17]. As a result, polyaniline is obtained in the form of its hydrochloride salt (emeraldine salt) which is a dark green color. In this work, iron oxide FeO was incorporated into the polymerization reaction medium after adjusting its pH to 8, therefore polyaniline in all the synthesized composites has the shape of the emeraldine base, which has low electrical conductivity properties.

The phase constitution of synthesized PAni + FeO composites with different aniline/FeO ratios before and after their use as catalysts in the electrohydrogenation of *p*-NBA was studied by means of XRD analysis. As an example, the X-ray diffraction patterns of PAni + FeO (1:1) - 2 composite are shown in Fig. 1.

It can be seen from the diffraction patterns that the phase constitution of the composite before electrohydrogenation (Fig. 1, *a*) contains the crystalline phases of the introduced wüstite (FeO) and magnetite (Fe_3O_4) in addition to the amorphous phase of the polymer. The intensity of the peaks corresponding to wüstite in the diffraction patterns of all composites is higher than the intensity of magnetite peaks, which indicates a higher content of FeO compared with Fe_3O_4. It should be noted that the initial FeO powder also contains magnetite in a smaller amount than wüstite. In the X-ray diffraction pattern of the composite, there is also one weak peak with an interplanar distance *d* = 2.70 Å relating to hematite (α-Fe_2O_3). That means that Fe_2O_3 oxide is present in small amounts in the phase constitution of PAni + FeO composites.

It can be seen from the XRD pattern of PAni + FeO (1:1) - 2 composite after the hydrogen saturation stage (Fig. 1, *b*) that already at this stage, crystalline phases of iron in the zero-valence state appear in the composite as a result of the electrochemical reduction of Fe^{2+} cations in FeO. This is confirmed by a decrease in the intensity of the iron oxide peaks. We can also note a certain relative decrease in the intensity of the peak at *d* = 2.53 Å, which belongs to magnetite. However, verification experiments with Fe_3O_4 powder deposited on a Cu cathode did not reveal its ability to effect the electrochemical reduction under the same conditions described in the Experimental section.

The XRD pattern of PAni + FeO (1:1) - 2 composite deposited on a Cu cathode after electrocatalytic hydrogenation of *p*-NBA (Fig. 1, *c*) is almost the same as the XRD pattern for the composite after the hydrogen saturation stage (Fig. 1, *b*), but with a higher peak for Fe^0 relatively to the FeO peak. Fe^0 crystalline phases with their distinctive peaks in the XRD patterns are present in all the composites after the hydrogenation process. However, there is no correlation between the increase in the amount of FeO introduced and the increase of metallic iron (Fig. 2, *a–d*).

The PAni + FeO (1:0,6) and PAni + FeO (1:1) composites show the highest content of reduced iron, according to the intensity of the peaks in their XRD patterns (Fig. 2, *a* and *c*). An increase in the amount of iron (II) oxide introduced into the polymer to an aniline ratio of 1:1.5 leads to the formation of crystalline phases of zero-valence iron with peaks of much lower intensity (Fig. 2, *d*). Because it is the Fe^0 metal particles that catalyze the hydrogenation of the nitro-aromatic compound under investigation, the electrocatalytic activity of the synthesized composites should depend on Fe^0 content.

According to the XRD pattern of PAni + FeO (1:1) - 2 composite deposited on a Pb cathode after electrocatalytic hydrogenation of

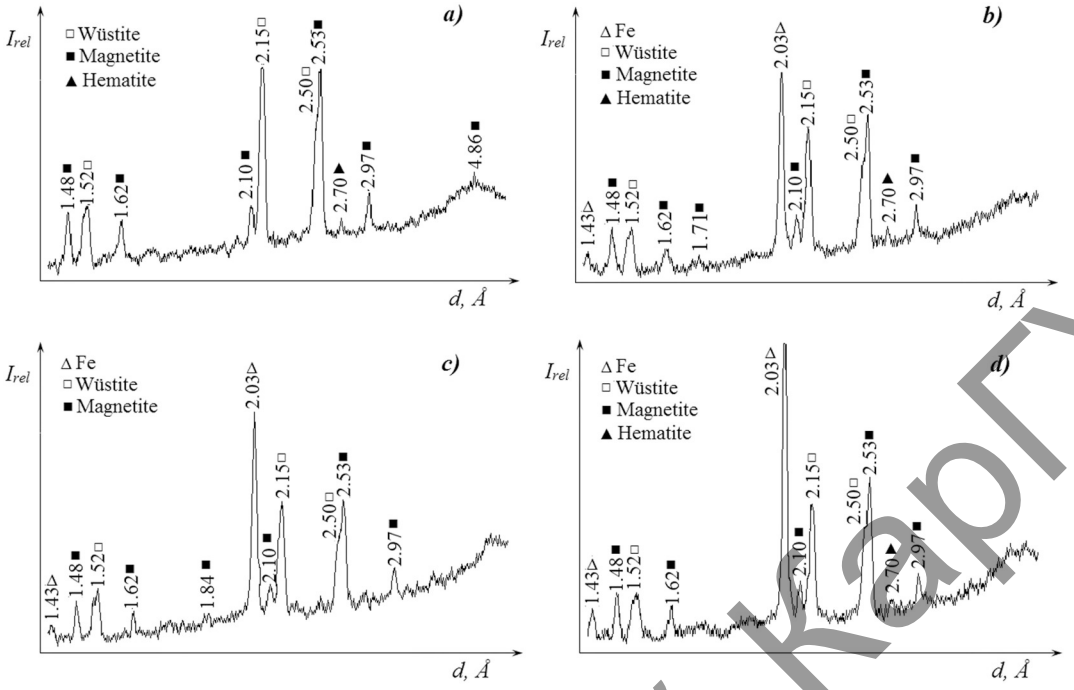

Fig. 1. XRD patterns for PAni + FeO (1:1) - 2 composite (*a*) before electrocatalytic hydrogenation of *p*-NBA; (*b*) after hydrogen saturation stage and (*c*) after electrocatalytic hydrogenation of *p*-NBA on the composite supporting Cu cathode and (*d*) Pb cathode.

p-NBA (Fig. 1, *d*), the content of iron crystalline phases relative to FeO becomes higher in this composite than in the composite deposited on a Cu cathode. This indicates that the electrochemical reduction of iron cations on a Pb cathode with a high hydrogen overvoltage is more complete than on a Cu cathode with a lower hydrogen overvoltage.

Looking at the SEM micrographs of PAni + FeO (1:1) composite before hydrogenation of *p*-NBA (Fig. 3, *a*), the particles of FeO powder, sonicated prior to their introduction into the polymer matrix, are clearly visible in the form of separate round particles with a diameter of ~1.0–3.0 μm and in clusters of two or more monoparticles. The polymer, PAni base, consists of chaotically located short nanotubes (80–100 nm in diameter) forming a rather loose structure of the polymer as a whole. Micrographs of this composite after its application in the electrocatalytic process (Fig. 3, *b*) show that the present iron-containing cluster formations also consist of coarse particles and smaller round ones. The polymer itself (in the form of the PAni base), like in the composite before electrohydrogenation, has a loose net structure and consists of short nanotubes with a diameter of

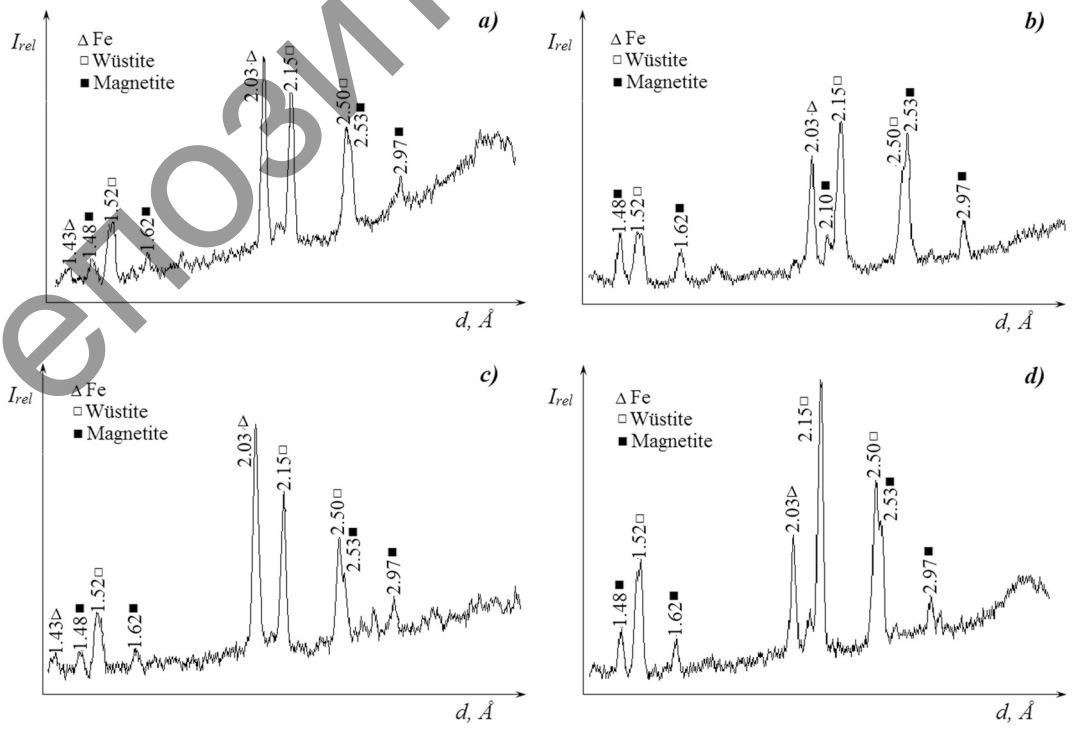

Fig. 2. XRD patterns for PAni + FeO composites with aniline/FeO ratios of (*a*) 1:0.6; (*b*) 1:1; (*c*) 1:0.8; and (*d*) 1:1.5 after electrocatalytic hydrogenation of *p*-NBA.

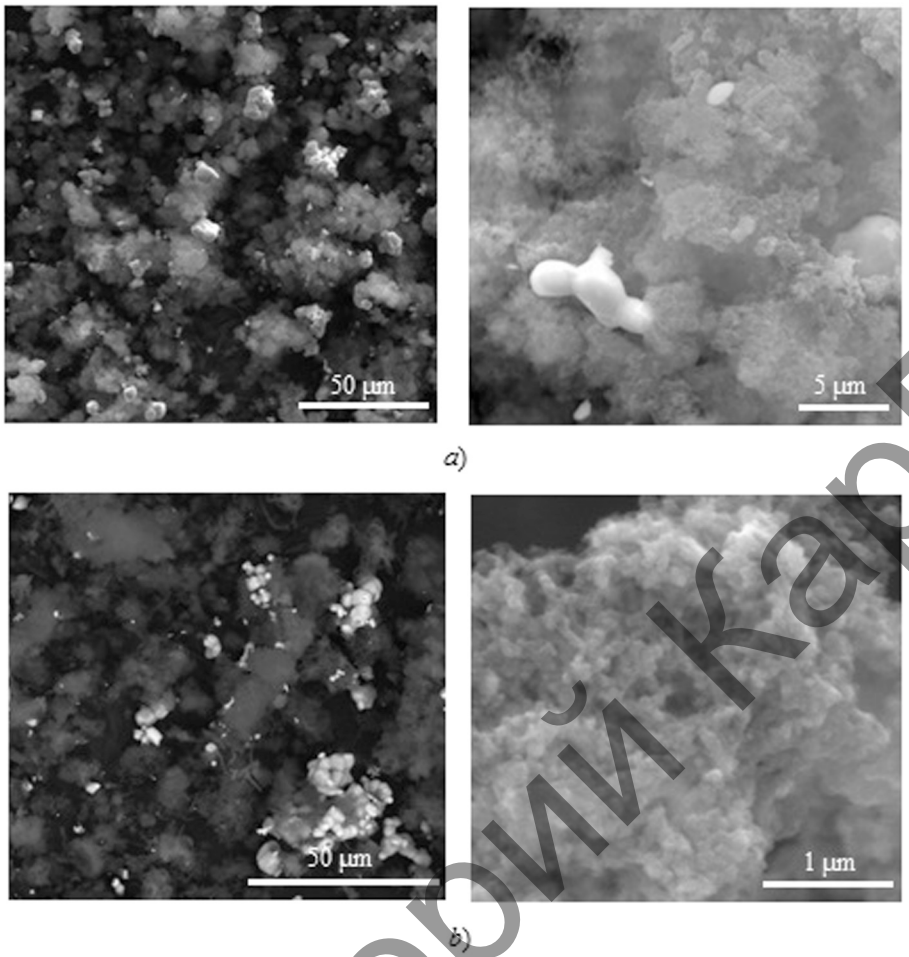

Fig. 3. SEM micrographs of PAni + FeO (1:1) composite (*a*) before and (*b*) after electrocatalytic hydrogenation of *p*-NBA.

~40–90 nm. At the same time, the presence of S and Cl chemical elements was detected on its surface, but in smaller amounts than in the composite before the electrohydrogenation process.

The synthesized PAni + FeO composites with various aniline/FeO ratios were deposited on a Cu cathode surface and used as catalysts in the electrochemical reduction of *p*-NBA (Table 1). For comparison, the results of the electrochemical reduction of *p*-NBA on Cu and Pb cathodes (without PAni composite) and electrocatalytic hydrogenation of *p*-NBA on PAni + FeO (1:1) - 2 composite using supporting Cu and Pb cathodes under the same conditions are shown in the Table. The values of the amount of electricity (*Q*) are calculated taking into account the duration of the separate hydrogen saturation stage (I) (measured with a time excess) and the electrohydrogenation stage (II). The current efficiency for stage II is determined from the relation Q_{II}(theor.) / Q_{II}(real.) · 100%, where Q_{II}(theor.) is corrected by taking into account the α values (the reduction of *p*-NBA is not complete).

From the data in Table 1 it follows that the electrochemical reduction (ER) of *p*-NBA (in the form of its sodium benzoate) on the Pb cathode with a high hydrogen overvoltage passes more intensively than on the Cu cathode with a low hydrogen overvoltage. A copper cathode with its ability to adsorb atomic hydrogen can participate both in electrochemical reduction of *p*-NBA (electronation-protonation mechanism (EP)) and in its electrocatalytic hydrogenation (ECH), promoting the formation of an amino product. On a Pb cathode, the mechanism of reduction should be the EP mechanism (the current is due to the electronation of *p*-NBA) and, therefore, the reduction should stopped at the *p*-hydroxylaminobenzoate (not reducible by electron transfer in a basic medium). The mechanisms of electrohydrogenation of nitroaromatic compounds were studied in detail in the works [18,19]. Perhaps the high values of the ER rate of *p*-NBA and its conversion on the Pb cathode (calculated with allowance for the volume of absorbed hydrogen) are due to side processes.

Regarding the ER of *p*-NBA on the Cu cathode, its hydrogenation rate and conversion with the use of PAni + FeO composites increase noticeably (compare entry 1 with entries 3–8, especially for composites with PAni/FeO ratios of 1:0.6 and 1:1 (entries 5, 7 and 8 respectively). The electrocatalytic hydrogenation of *p*-NBA on the PAN + Fe^0 + FeO + Fe_3O_4 composite formed from PAni + FeO (1:1) - 2 composite deposited on the Pb cathode (Fig. 2, *d*) is carried out at a higher rate, greater hydrogen utilization coefficient, but close to other parameters of the ER process on the Pb cathode (entries 9 and 2).

Comparison of the results of the ECH of *p*-NBA with the participation of the PAN + FeO (1:1) - 2 composite deposited on Cu and Pb cathodes (entries 8 and 9 in Table 1) shows the same values of the current efficiency, slightly differing reaction rates and hydrogen utilization coefficients, and a slightly higher conversion of *p*-NBK (α) on a copper cathode. The data suggest that the support (Cu or Pb) has a negligible influence on the ECH process. This is in a good agreement with the conclusions of our work [14] dedicated to copper-containing PAni composites.

The iron content (in the forms of FeO and Fe_3O_4) in 1 g of initial PAni + FeO composites is rather high. However, the increase in the average hydrogenation rate of *p*-NBA is not influenced significantly by this parameter. The average hydrogenation rate does depend on the amount of metallic iron in the composite and on its accessibility for the adsorption the organic compound. Apparently, aniline/FeO ratios of 1:0.6 (entry 5) and 1:1 (entries 7, 8, and 9) are optimal for the best reduction of iron cations in FeO oxide under the given conditions. The

Table 2
Magnetic characteristics of PAni + FeO (1:0.6) composite.

Composite	M_S, emu/g	M_0, emu/g	H_c, Oe
1	11.5	1.26	177
2	15.3	1.26	160

current efficiency is also the highest for these three entries.

For PAni + FeO (1: 1) - 2 composites before and after the electrohydrogenation process, the specific surface area values were determined (BET method, Sorbi MS instrument), and found to be 31.3 m^2/g and 23.7 m^2/g, respectively. It is obvious that the forming PAni + Fe^0 + FeO + Fe_3O_4 cathodic coating with a large specific surface affects the hydrogen overvoltage potential, which decreases in alkaline catholyte solution [20,21], and electrohydrogenation of *p*-NBA as a whole.

In spite of the fact that, in this work, the electrohydrogenation products were not isolated and identified, it can be assumed, referring to the studies carried out in [18,19], that the electrohydrogenation of *p*-NBA in an alkaline medium on the novel PAni + Fe^0 + FeO + Fe_3O_4 cathodic coating with a large specific surface area includes both mechanisms (EP and ECH), and the main product is *p*-aminobenzoic acid.

The powders of the initial PAni + FeO + Fe_3O_4 composites deposited on a horizontally located cathode are maintained on its surface by an out-cell magnet. In the course of the studies, it was observed that composites after electrohydrogenation of *p*-NBA have better magnetic properties than the initial composites. Table 2 reports the magnetic properties of the composite PAni + FeO (1:0.6) before (*1*) and after (*2*) electrohydrogenation of *p*-NBA: M_S is the saturation magnetization, M_0 the residual magnetization, and H_c the coercive force. This composite was chosen because of its good performance as an electrocatalyst (see Table 1, entry 5).

According to the data in Table 2, composite *2* is characterized by a higher saturation magnetization and lower coercive force than composite *1*. Evidently this is facilitated by the appearance of crystalline phases of metallic iron in the constitution of composite *2*. The obtained iron- and iron-oxides-containing PAni composites with these magnetic characteristics can be classed as soft magnetic materials having many applications in a variety of fields.

4. Conclusions

PAni + FeO + Fe_3O_4 composites were prepared by the introduction of iron (II) oxide into the reaction medium of oxidative polymerization of aniline. The composites deposited as a powder on a Cu cathode were electroactive in the electrochemical reduction of *p*-nitrobenzoic acid in aqueous NaOH. The electrocatalytic activity was evidenced by the hydrogenolysis of the intermediate *p*-hydroxylaminobenzoate to the aminobenzoate and was attributed to the formation of iron in the zero-valence state as a result of the electrochemical reduction of Fe^{2+} cations of FeO. In addition, the magnetic properties of PAni + FeO (1:0.6) composite before and after the electrohydrogenation process were studied, and suggest that the iron- and iron oxides-containing PAni composites obtained can be classed as soft magnetic materials.

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