Int. J. Electrochem. Sci., 13 **(2018)** 424 – 432, doi: 10.20964/2018.01.13

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Preparation and Characterization of POAP/Fe_2O_3 Magnetic Nanocomposite in One-Step Method

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Received: 9 February 2017 / *Accepted:* 13 March 2017 / *Online Published:* 1 December 2017

In this paper, composite of poly ortho-aminophenol containing Fe_2O_3 with nanosize particles was synthesized by a simple and one-step method. The characteristics of products such as morphology, magnetic properties and electrical conductivity were studied. The scanning electron microscopy (SEM) and X-Ray Diffraction (XRD) studies indicated controllable morphology and the effect of the presence of Fe_2O_3 phase in the nanocomposit. The synthesized nanocomposite has good conductivity and magnetic properties, depended on the presence of iron oxide nanoparticles in the range of 30-60 nm. For the conducting nanocomposite the saturation magnetization (M_S) was 0.539 emu/g and the electrical conductivity was 0.37 S/cm, which are measured by vibrating sample magnetometer (VSM) and four-probe technique, respectively.

Keywords: Conducting polymer, Poly ortho-aminophenol, Iron oxide, Nanocomposites.

1. INTRODUCTION

Electronically conducting polymers are generally used by material researchers extensively, because of their wide range of applications, often for their low cost, light weight and good mechanical properties [1-3]. Conducting polymers have a wide range of possible applications such as conductive paints [4], optical devices [5], sensors, biomedical applications [6], removal of heavy metals from water and wastewater [7], and polymer solar cells [8, 9]. Poly ortho-aminophenol (POAP) exhibits a number of interesting properties such as unique electrical, optical and photoelectrical properties, high conductivity, relatively good environmental stability, and wide technological applications [10-11]. Composite materials based on magnetic and/or conducting materials have attracted the attention of scientists for their applications [12] in many fields, including corrosion protection, organic light emitting diodes (OLED), secondary rechargeable batteries and sensors for new or enhanced physical

properties, environmental stability, low cost and easy of synthesis [13-15]. Incorporation of magnetic nanosize metal oxides in conducting polymer matrix can lead to create materials, which can be designed for high-tech applications. Generally, organic materials having an electrical or magnetic function have attracted interests due to their unique properties and numerous application in technology. The nanocomposites of conducting polymer have many possible in electromagnetic technological applications. These electromagnetic composite can be used for therapeutic or analytical purposes such as release of a drug in a specific site of the body [16-18], electromagnetic interference shielding material in the form of paints or coatings [19], supercapacitor applications [20], optical and antibacterial applications [21], dyes removal [22], wastewater treatment [23]. Different methods have been reported for the synthesis of iron oxide nanocomposites. Shahrousvand et al in (2017) reported the magnetite polyurethane nanocomposites as a potential choice for cell therapy and tissue engineering [16]. Chanhom et al in (2017) demonstrated bactericidal activity of the titania-silica-iron oxide nanocomposites [24]. Sheshmani et al in (2017) used magnetic graphene oxide-ferrite nanocomposites for oxidative decomposition of Remazol Black B [25]. The presence of magnetic filler nanoparticles in the polymer matrix, led to enhancement of magnetic and transport properties. Magnetic materials based on iron oxides have attracted a great interest because of their novel physical properties and potential applications [26-30]. Numerous studies have reported the composite of iron oxide with conductive polymers [31-33], but to the best of our knowledge no one has offered POAP and Fe_2O_3 composites. Because of unique structure, environmental stability, relatively low cost, and easy process ability of POAP, the nanocomposite of POAP and Fe_2O_3 are studied here.

In this paper, we reported the synthesis of POAP/Fe_2O_3 nanocomposites and characterized the morphology, magnetic behavior and electrical conductivity of this composite. The nanocomposite has been prepared by the electropolymerization of ortho -aminophenol in the presence of Fe_2O_3 nanoparticles.

2. MATERIALS AND METHODS

The chemicals used in this work were obtained from Merck Chemical Co in analytical grades and were used without any further purification. Solutions were prepared using deionized water. The electrochemical tests were performed using a conventional three-electrode cell powered by an Autolab potentiostat/galvanostat and a frequency response analyzer (Metrohm, model 12/30/302, The Netherlands). A stainless steel panel was used as the working electrode and a platinum wire as auxiliary electrode and Ag/AgCl was used as the working electrode. The morphology of the electrosynthesized conductive polymers was analyzed using field emission scanning electron microanalyzer (KYKY-FESEM 3200.1) The X-ray diffraction patterns were taken with an x-ray diffractometer (Shimadzu XRD 6000, Japan) using Kα radiation of copper with wavelength of 1.54 A and step size of 2θ 0.02°. The magnetic measurements of Fe_2O_3 as well as conducting POAP/Fe_2O_3 nanocomposite were carried out using vibrating sample magnetometer (Lakeshore VSM 7200, USA).

2.1. Synthesis of POAP/ Fe_2O_3

The Fe_2O_3 nanoparticle was produced under galvanostatic mode at the pulse current of 20 mA/cm^2 by oxidation of 0.005M $FeSO_4$ aqueous solutions [34]. Poly (ortho-aminophenol) electrodeposited on the cleaned steel panel electrode by pulsed current electropolymerization from an aqueous solution containing 0.02M ortho-aminophenol, 0.04M sodium dodecyl sulfate and 0.6 M perchloric acid with the pulse current of 10 mA/cm^2, pulse time and relaxation time of 0.5 s. Before each experiment, the bare steel panel electrode was polished with 0.05 μm $\propto$-Al_2O_3 on a piece of leather and thoroughly washed with distilled water and then rinsed ultrasonically in ethanol and water for 5 min. The POAP/Fe_2O_3 nanocomposite was fabricated by the same procedure, but with the addition of 10 mg Fe_2O_3 nanoparticles. Sodium dodecyl sulfate was used as an additive in order to suspend particles and improve the stability and electroactivity of the resulting films.

3. RESULTS AND DISCUSSION

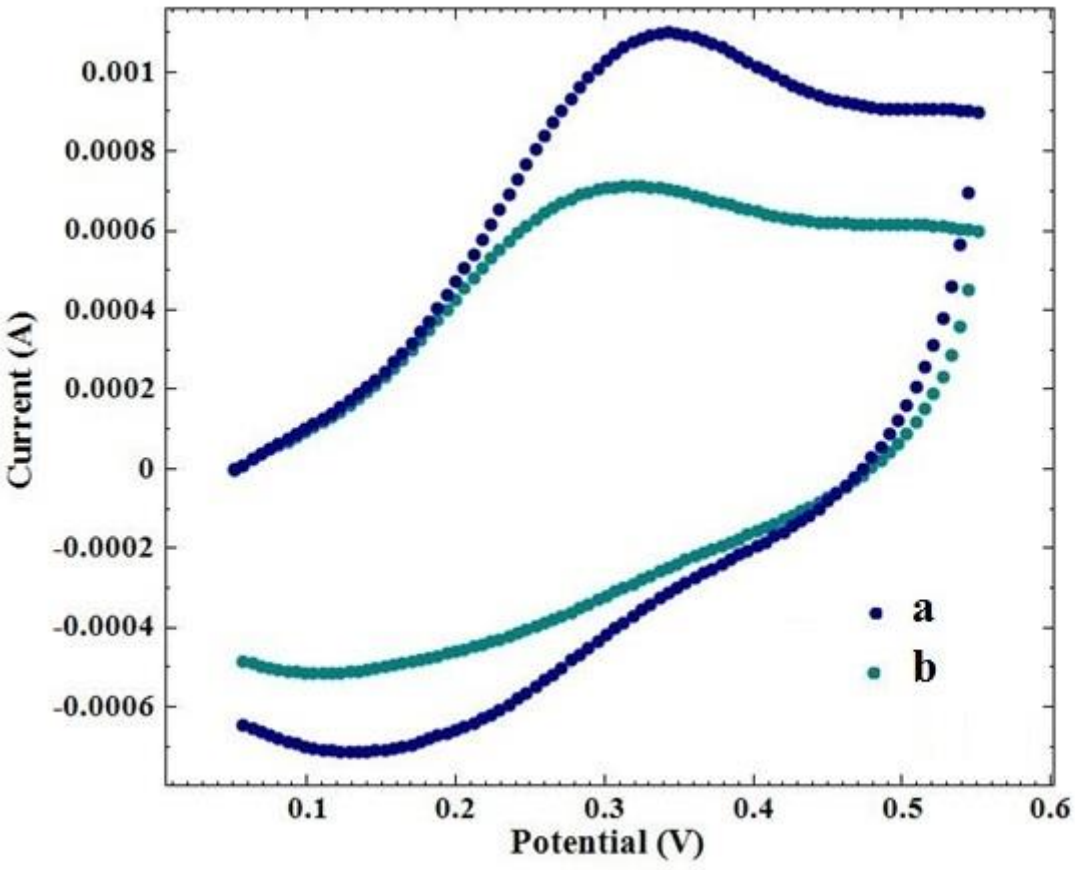

Figure 1. Cyclic voltammograms of (a) POAP/Fe_2O_3 and (b) POAP obtained in 0.04M sodium dodecyl sulfate and 0.6 M $HClO_4$ solution at the scan rate of 50 mVs^{-1}.

The Synthesis of POAP/Fe_2O_3 was carried out using pulsed current electrodeposition technique in aqueous solution to bring certain changes in the properties of POAP. First, the effective parameters,

which include, pulse current amplitude, pulse time (t_{on}) and relaxation time (t_{off}), the weight ratio of Fe_2O_3 to ortho-aminophenol and the temperature of the solution were optimized during experiments by the "one at a time" method to produce uniform and more stable and strength nanocomposite. The pulse currents from 1-100 mA/cm^2 were applied to the electrochemical cell. The strength of nanocomposite was poor when the pulse current increased from 10 mA/cm^2, but lower currents was not enough to occur the electrochemical polymerization. So 10 mA/cm^2 was chosen as optimal pulse current. The pulse time equal to relaxation time was changed from 0.05-1 s. In smaller times the relaxation time was too short to allow nucleation growth and the particle size was increased. The stable nanocomposite with smaller nanoparticles was formed in 0.5 s pulse time. Then the syntheses were carried out at different temperatures of 25, 45, 70 ºC. The higher temperature did not change the yield or strength of nanocomposite and the room temperature was set as optimum.

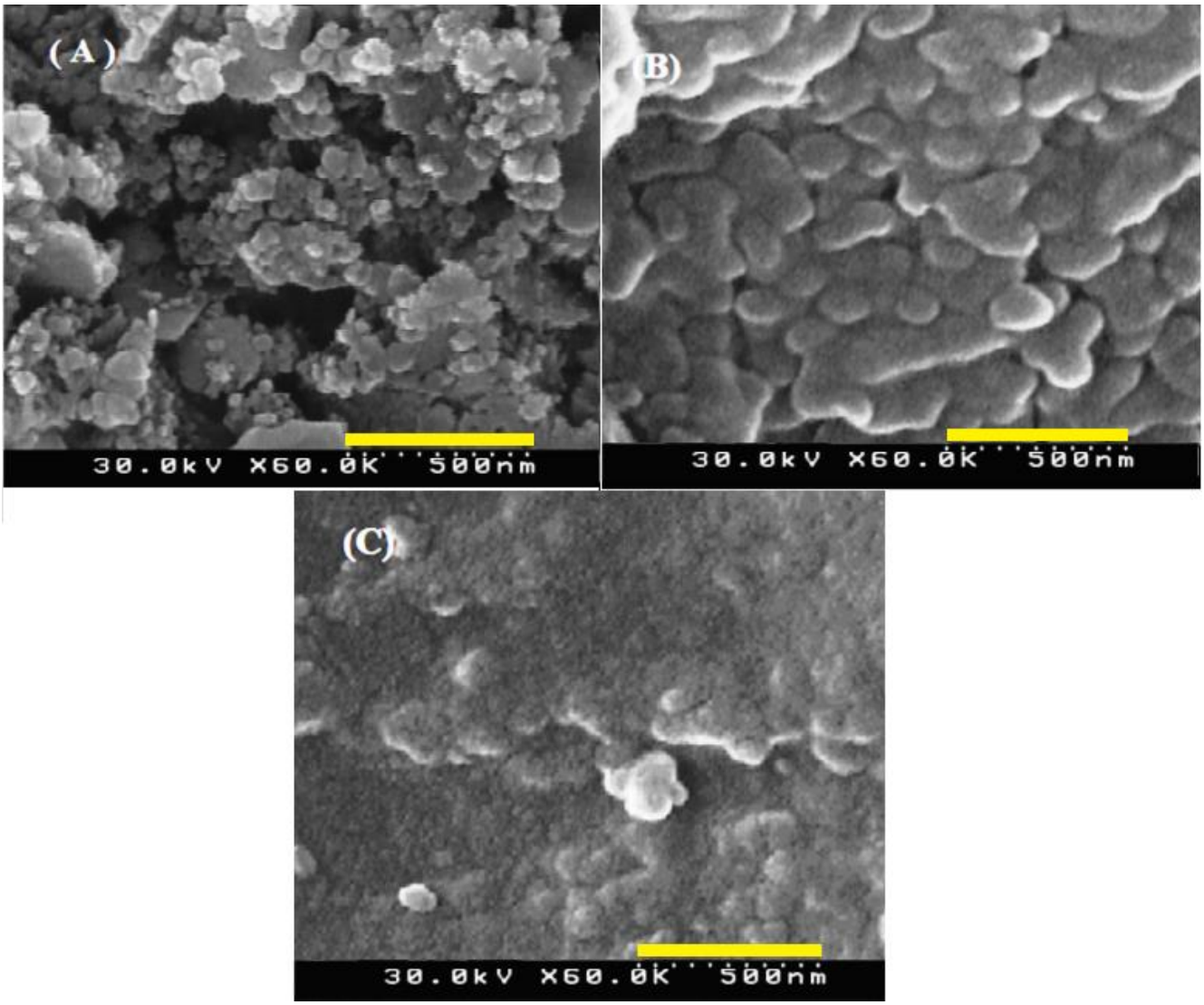

Figure 2. SEM images of Fe_2O_3 (A), POAP (B) POAP/Fe_2O_3 (C) synthesized by pulse current electrodeposition.

To clarify the effects of Fe_2O_3 on the properties of POAP films, electrochemical performance of composite films was evaluated by taking CV voltammograms in 0.6 M HClO4, and 0.04M sodium dodecyl sulfate in Fig. 1. As it can be seen, the voltammetric behavior of both films is similar and the wave currents of the POAP/Fe_2O_3 films showed a couple of strong and broad oxidation and reduction than that of the pure POAP films. However, when electropolymerization of POAP was carried out in the presence of Fe_2O_3 nanoparticles suspended in the surfactant medium, electrochemical behavior shows shifting of peak potential values, which displays the incorporation of Fe_2O_3 in the polymer backbone. The shifting of characteristic redox peaks can be assigned to the incorporation of Fe_2O_3 particles in the POAP matrix.

Figure 2 indicates the SEM images of POAP, Fe_2O_3, and POAP/Fe_2O_3. As can be seen, the morphology of POAP and POAP/Fe_2O_3 are quite different from each other, indicating that the entrance of Fe_2O_3 nanoparticles with the size of 30-60 nm into POAP, changes the structure of the polymer and the nanocomposite contains iron oxide nanoparticles of 30-60 nm.

For further investigation, x-ray diffraction patterns of POAP/Fe_2O_3nanocomposite were recorded (Fig. 3). As seen in figure 3, the crystalline nature of the nanoparticles is corroborated by electron diffraction patterns. The main peaks for Fe_2O_3 were observed at 2θ of 38°, 44°, and 64° which matches to the standard XRD pattern of Fe_2O_3. The observed peaks of Fe_2O_3 in all the nanocompositions of POAP with Fe_2O_3 indicate the presence of iron oxide nanoparticles in the polymer matrix and the intensity of peaks increase when the ratio of iron oxide increases. The presence of POAP and its semicrystalline nature is confirmed by the broad peaks at 2θ of 20°, and 40°.

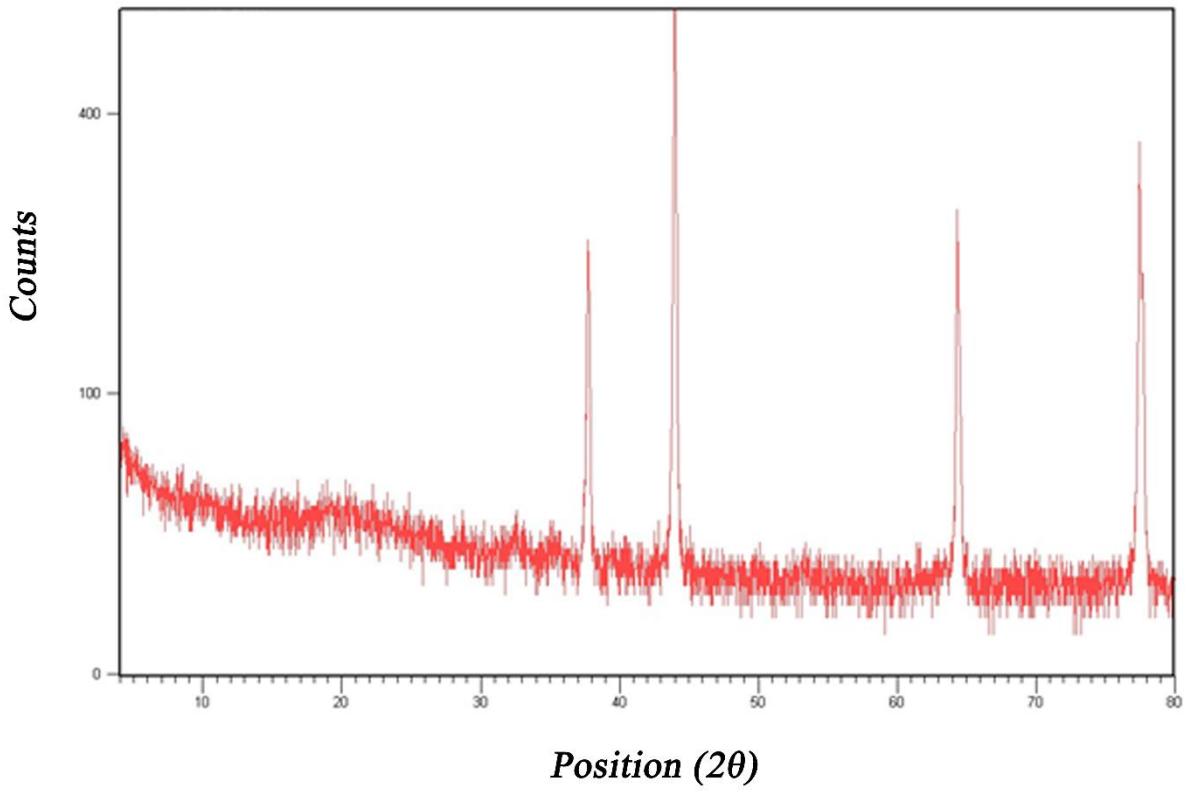

Figure 3. XRD pattern of synthesized POAP/Fe_2O_3 nanocomposite.

Table 1. The effect of Fe_2O_3 content in conductivity of POAP/Fe_2O_3 nanocomposite

%Fe_2O_3 Content	Conductivity (σ S/cm)
0	0.10
26.9	0.28
42.4	0.37
52.4	0.07

The electrical conductivity is one of the important parameters of conducting polymers. The results of conductivity measurements by direct four probe method at room temperature for POAP and POAP/Fe_2O_3 in Table 1, showed that with increase of weight ratio of Fe_2O_3 nanopartices to the monomer in the polymer matrix, the conductivity of nanocomposites differs. As can be seen the electrical conductivity of nanocomposite related to the type and amount of additive, because the type and size of additives influence the amount of electrical conductivity. The expected conductivity is due to the incorporation of Fe_2O_3 nanoparticles in the polymer matrix. Different models have been proposed in order to show the conductivity variations of conducting polymers. The studies show that best model explained by variable range hopping model which follows Mott's equation [35]. The maximum conductivity is achieved in 42.4% of Fe_2O_3 content (Fig. 4), but more than this value had a contrary effect and decreased the conductivity of nanoparticles.

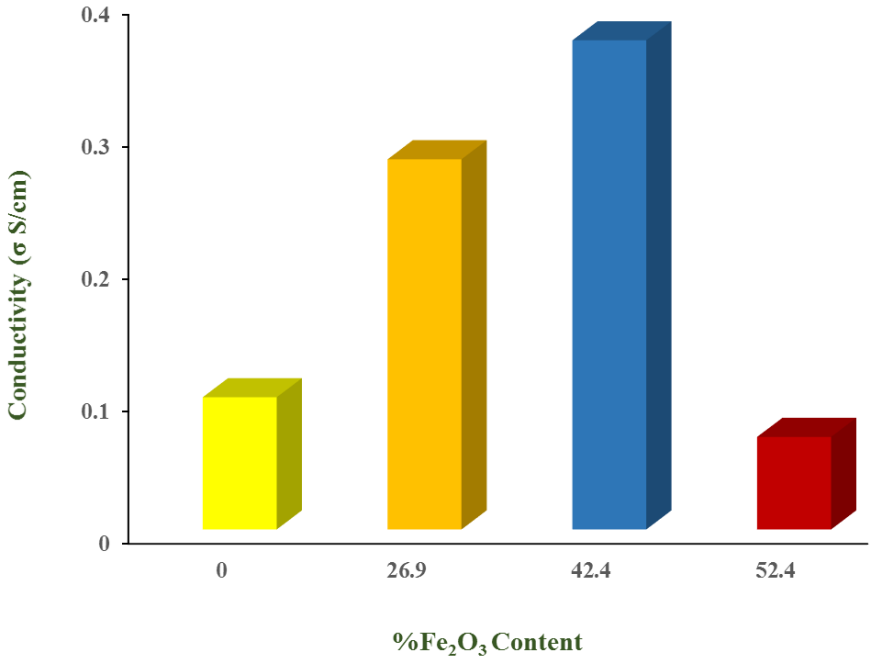

Figure 4. The effect of %Fe_2O_3 content in conductivity of POAP/Fe_2O_3 nanocomposite

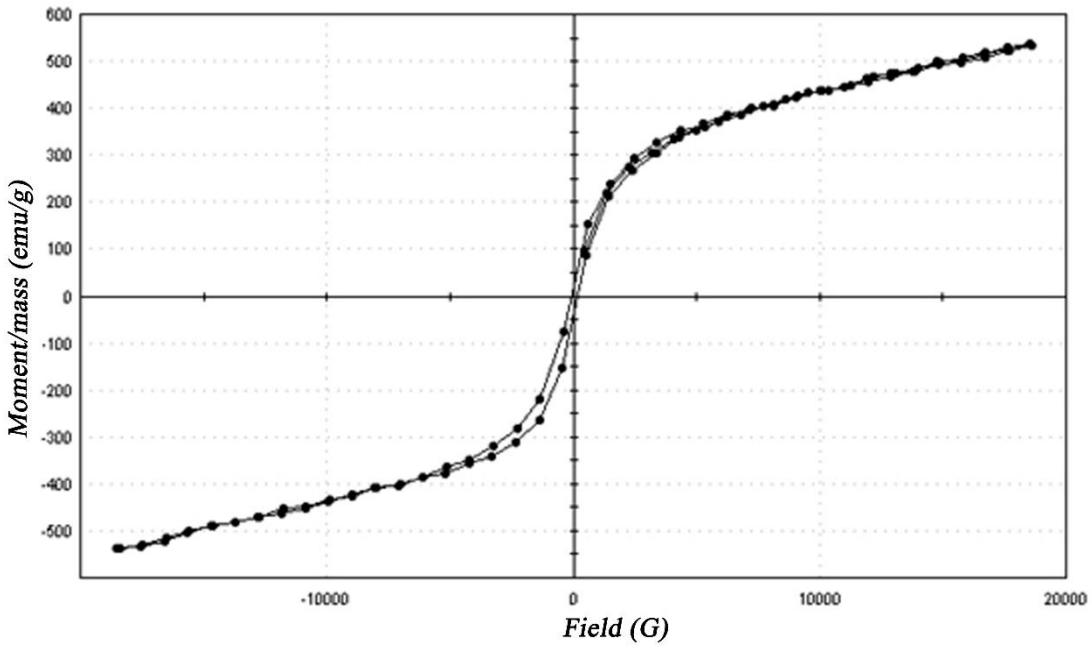

Figure 5. The (M-H) curve of synthesized POAP/Fe_2O_3

It is known that the magnetic properties of nancomposites are highly dependent on many factors, including the size of nanoparticles incorporated in it and the shape of nanocomposite [36]. Fig. 5 displays the room temperature magnetization curve of POAP/Fe_2O_3. The saturation magnetization (M_s) at the maximum applied magnetic field was 0.539 emu/g while that of Fe_2O_3 was 75 emu/g.

Table 2. Comparison of iron oxide effects on conductivity and saturation magnetization of nanocomposite.

Sample	**%Fe_2O_3 Content**	**Conductivity (σ S/cm)**	**Saturation magnetization (M_s emu/g)**	**Reference**
POAP/α-Fe_2O_3	42.4	0.37	0.539	This work
PAni/Fe_2O_3	50	6.8×10^{-6}	*	[39]
PAni/γ-Fe_2O_3	66.6	0.46	11.7	[32]
PAni/ γ-Fe_2O_3	60	0.8	15.2	[33]
PAni/ γ-Fe_2O_3	20.8	180	22	[40]

*Not mentioned

To the best of our knowledge POAP has not doped by α-Fe_2O_3 but the same studies were done for Poly aniline (PAni) doped by γ-Fe_2O_3, so we compared the effects of iron oxide presence in Conductivity and Saturation magnetization of polymer matrix of PAni in Table 2. As is clear from the data table 2, the electrical conductivity and saturation magnetization of nanocomposites depend on the amount of iron oxide. Zhang et al in (2010) reported the magnetic properties of PAni nanocomposites depending on the amount of iron oxide nanoparticles [29]. Magnetic and conductivity studies of Singh

et al in (2010) [32] demonstrated that the conducting ferromagnetic composite possesses saturation magnetization (M_S) value of 26.9 emu g^{-1} and conductivity of the order of 0.46 S cm^{-1}. They observed that the presence of the nanosized γ-Fe_2O_3 in the polyaniline/ TiO_2 matrix affects the electromagnetic shielding property of the composite. In general it can be said interactions between ferrite particles and polymer matrix determine the behavior of nanocomposite, and the material magnetic properties could be controlled through the nanoparticles to polymer ratio [37]. Varshney et al in (2012) synthesized ferromagnetic iron oxide-polypyrrole with electrical conductivity of the order of 10^{-2} S/cm and saturation magnetization (M_s) value of 35 emu/g which Fe_2O_3 Content was 75 % [38].

4. CONCLUSION

The POAP/Fe_2O_3 nanocomposite with both electrical conductance and magnetic properties was synthesized by a new simple one–step method. The synthesized nanocomposite possessed magnetic properties and the saturation magnetization was 0.539 emu/g. The electrical conductivity of synthesized nanocomposite depends on Fe_2O_3 content and in optimal 42.4% was 0.37 S/cm. Electrochemical properties of films were investigated by using cyclic voltammetry. The surface morphology of POAP films was revealed by using SEM. The XRD pattern has shown the presence of Fe_2O_3 nanoparticles in the POAP matrix which is in agreement with the electrochemical results. The results show the presence of particle–matrix interactions and the material magnetic properties could be controlled through the nanoparticles to polymer ratio.

ACKNOWLEDGEMENT
The authors would like to express their deep gratitude to the Payame Noor University and Iranian Nano Council for supporting this work.

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