

## Preparation and Characterization of POAP/Fe<sub>2</sub>O<sub>3</sub> Magnetic Nanocomposite in One-Step Method

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In this paper, composite of poly ortho-aminophenol containing Fe<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub> 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<sub>S</sub>) 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.

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**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  $\text{Fe}_2\text{O}_3$  composites. Because of unique structure, environmental stability, relatively low cost, and easy process ability of POAP, the nanocomposite of POAP and  $\text{Fe}_2\text{O}_3$  are studied here.

In this paper, we reported the synthesis of POAP/ $\text{Fe}_2\text{O}_3$  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  $\text{Fe}_2\text{O}_3$  nanoparticles.

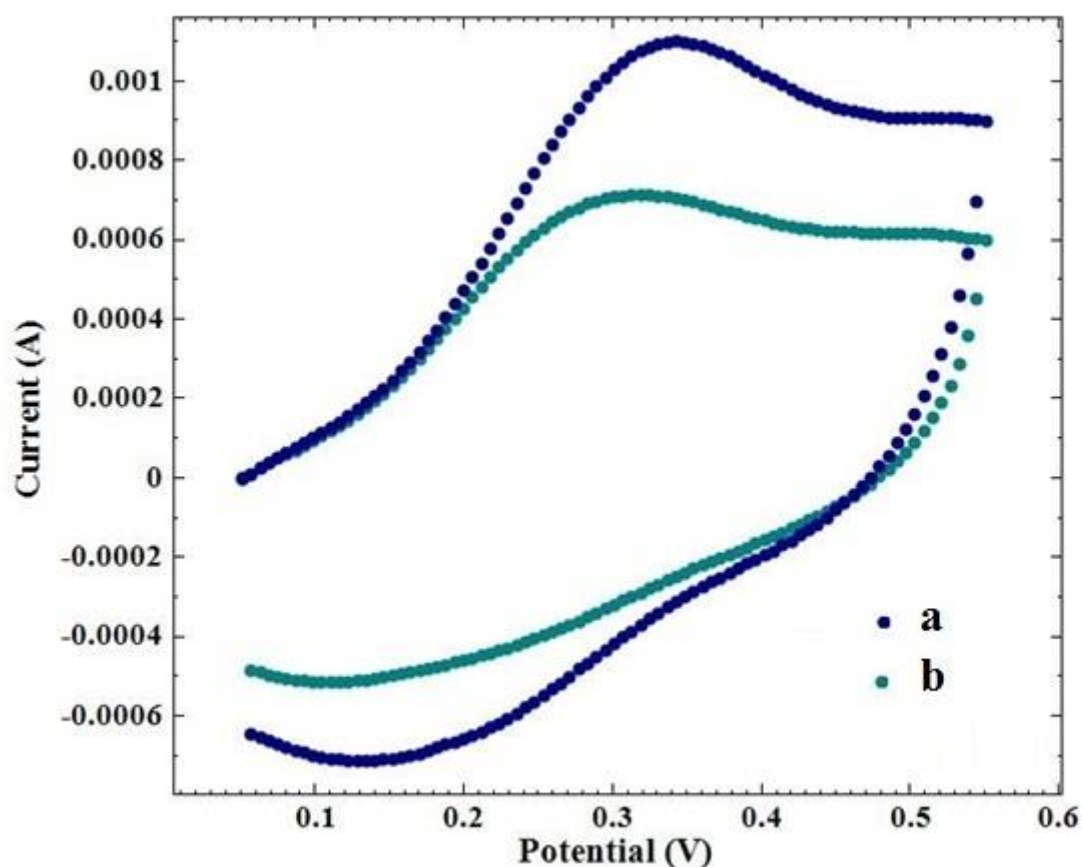
## 2. MATERIALS AND METHODS

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  $K\alpha$  radiation of copper with wavelength of 1.54 Å and step size of  $2\theta$  0.02°. The magnetic measurements of  $\text{Fe}_2\text{O}_3$  as well as conducting POAP/ $\text{Fe}_2\text{O}_3$  nanocomposite were carried out using vibrating sample magnetometer (Lakeshore VSM 7200, USA).

### 2.1. Synthesis of POAP/Fe<sub>2</sub>O<sub>3</sub>

The Fe<sub>2</sub>O<sub>3</sub> nanoparticle was produced under galvanostatic mode at the pulse current of 20 mA/cm<sup>2</sup> by oxidation of 0.005M FeSO<sub>4</sub> 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<sup>2</sup>, pulse time and relaxation time of 0.5 s. Before each experiment, the bare steel panel electrode was polished with 0.05 μm α-Al<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub> nanocomposite was fabricated by the same procedure, but with the addition of 10 mg Fe<sub>2</sub>O<sub>3</sub> nanoparticles. Sodium dodecyl sulfate was used as an additive in order to suspend particles and improve the stability and electroactivity of the resulting films.

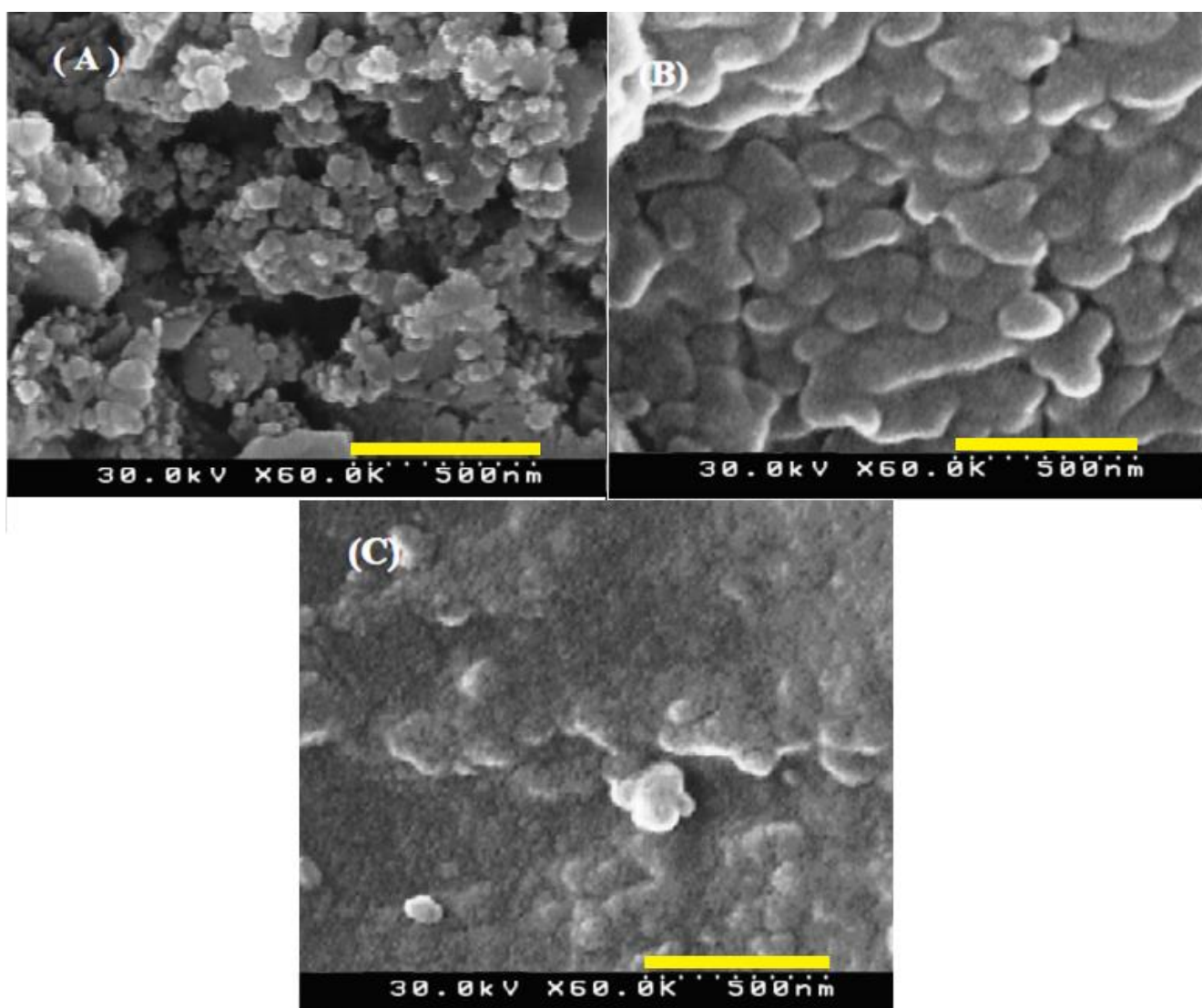
## 3. RESULTS AND DISCUSSION



**Figure 1.** Cyclic voltammograms of (a) POAP/Fe<sub>2</sub>O<sub>3</sub> and (b) POAP obtained in 0.04M sodium dodecyl sulfate and 0.6 M HClO<sub>4</sub> solution at the scan rate of 50 mVs<sup>-1</sup>.

The Synthesis of POAP/Fe<sub>2</sub>O<sub>3</sub> 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 °C. The higher temperature did not change the yield or strength of nanocomposite and the room temperature was set as optimum.

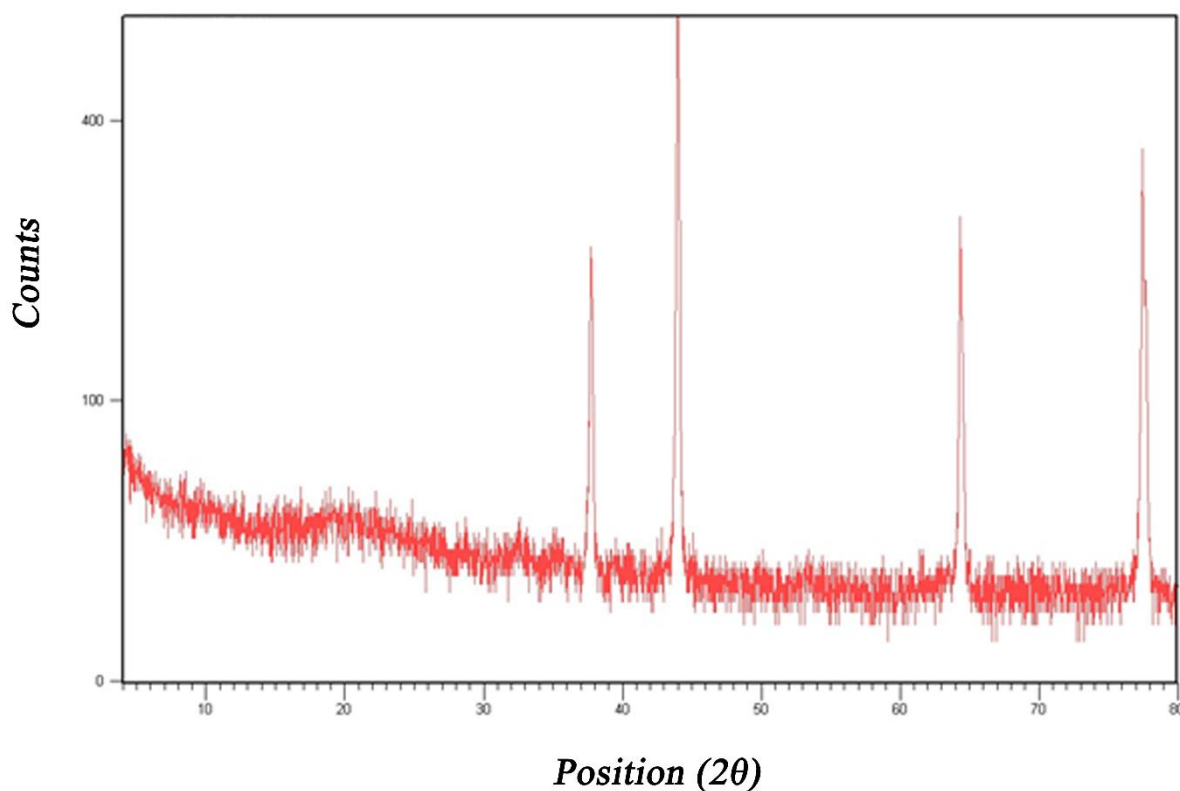


**Figure 2.** SEM images of  $Fe_2O_3$  (A), POAP (B) POAP/ $Fe_2O_3$  (C) synthesized by pulse current electrodeposition.

To clarify the effects of  $\text{Fe}_2\text{O}_3$  on the properties of POAP films, electrochemical performance of composite films was evaluated by taking CV voltammograms in 0.6 M  $\text{HClO}_4$ , 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/ $\text{Fe}_2\text{O}_3$  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  $\text{Fe}_2\text{O}_3$  nanoparticles suspended in the surfactant medium, electrochemical behavior shows shifting of peak potential values, which displays the incorporation of  $\text{Fe}_2\text{O}_3$  in the polymer backbone. The shifting of characteristic redox peaks can be assigned to the incorporation of  $\text{Fe}_2\text{O}_3$  particles in the POAP matrix.

Figure 2 indicates the SEM images of POAP,  $\text{Fe}_2\text{O}_3$ , and POAP/ $\text{Fe}_2\text{O}_3$ . As can be seen, the morphology of POAP and POAP/ $\text{Fe}_2\text{O}_3$  are quite different from each other, indicating that the entrance of  $\text{Fe}_2\text{O}_3$  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/ $\text{Fe}_2\text{O}_3$  nanocomposite 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  $\text{Fe}_2\text{O}_3$  were observed at  $2\theta$  of  $38^\circ$ ,  $44^\circ$ , and  $64^\circ$  which matches to the standard XRD pattern of  $\text{Fe}_2\text{O}_3$ . The observed peaks of  $\text{Fe}_2\text{O}_3$  in all the nanocompositions of POAP with  $\text{Fe}_2\text{O}_3$  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  $2\theta$  of  $20^\circ$ , and  $40^\circ$ .

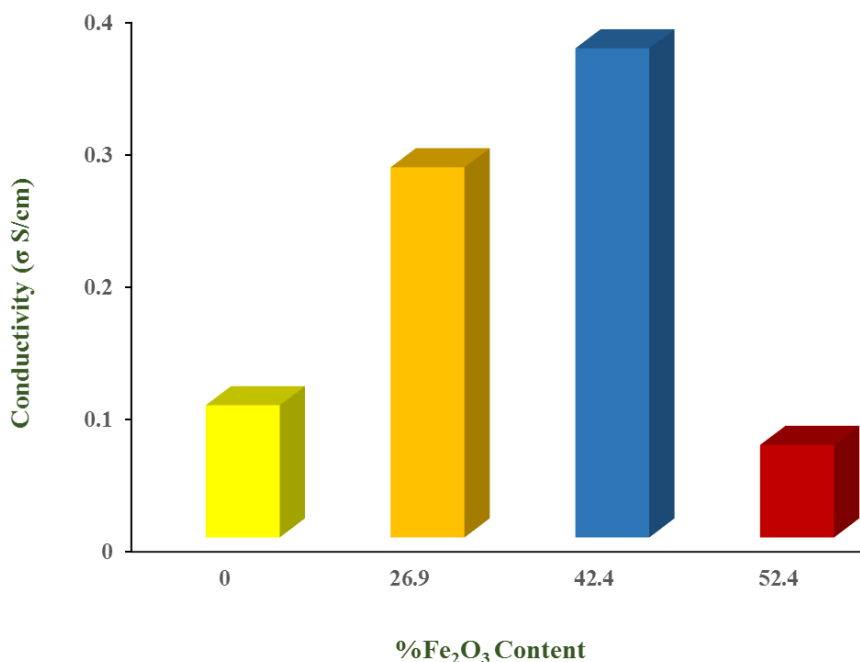


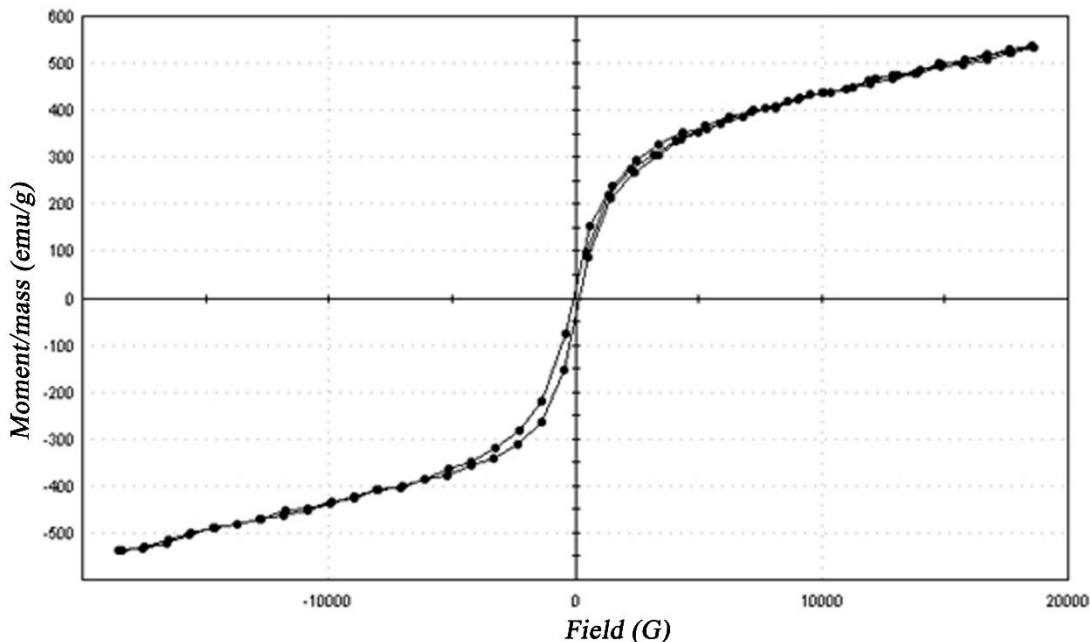
**Figure 3.** XRD pattern of synthesized POAP/ $\text{Fe}_2\text{O}_3$  nanocomposite.

**Table 1.** The effect of Fe<sub>2</sub>O<sub>3</sub> content in conductivity of POAP/Fe<sub>2</sub>O<sub>3</sub> nanocomposite

%Fe <sub>2</sub> O <sub>3</sub> Content	Conductivity ( $\sigma$ 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<sub>2</sub>O<sub>3</sub> in Table 1, showed that with increase of weight ratio of Fe<sub>2</sub>O<sub>3</sub> nanoparticles 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<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub> content (Fig. 4), but more than this value had a contrary effect and decreased the conductivity of nanoparticles.

**Figure 4.** The effect of %Fe<sub>2</sub>O<sub>3</sub> content in conductivity of POAP/Fe<sub>2</sub>O<sub>3</sub> nanocomposite



**Figure 5.** The (M-H) curve of synthesized POAP/Fe<sub>2</sub>O<sub>3</sub>

It is known that the magnetic properties of nanocomposites 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<sub>2</sub>O<sub>3</sub>. The saturation magnetization ( $M_s$ ) at the maximum applied magnetic field was 0.539 emu/g while that of Fe<sub>2</sub>O<sub>3</sub> was 75 emu/g.

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

Sample	%Fe <sub>2</sub> O <sub>3</sub> Content	Conductivity ( $\sigma$ S/cm)	Saturation magnetization ( $M_s$ emu/g)	Reference
POAP/ $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	42.4	0.37	0.539	This work
PAni/Fe <sub>2</sub> O <sub>3</sub>	50	$6.8 \times 10^{-6}$	*	[39]
PAni/ $\gamma$ -Fe <sub>2</sub> O <sub>3</sub>	66.6	0.46	11.7	[32]
PAni/ $\gamma$ -Fe <sub>2</sub> O <sub>3</sub>	60	0.8	15.2	[33]
PAni/ $\gamma$ -Fe <sub>2</sub> O <sub>3</sub>	20.8	180	22	[40]

\*Not mentioned

To the best of our knowledge POAP has not doped by  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> but the same studies were done for Poly aniline (PAni) doped by  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, 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  $26.9 \text{ emu g}^{-1}$  and conductivity of the order of  $0.46 \text{ S cm}^{-1}$ . They observed that the presence of the nanosized  $\gamma\text{-Fe}_2\text{O}_3$  in the polyaniline/  $\text{TiO}_2$  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  $10^{-2} \text{ S/cm}$  and saturation magnetization ( $M_s$ ) value of  $35 \text{ emu/g}$  which  $\text{Fe}_2\text{O}_3$  Content was 75 % [38].

#### 4. CONCLUSION

The POAP/ $\text{Fe}_2\text{O}_3$  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  $0.539 \text{ emu/g}$ . The electrical conductivity of synthesized nanocomposite depends on  $\text{Fe}_2\text{O}_3$  content and in optimal 42.4% was  $0.37 \text{ S/cm}$ . 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  $\text{Fe}_2\text{O}_3$  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.

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