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Comparative Studies of Chemically Synthesized Polymers Aniline and o-Toluidine Nanocomposite Using Algerian Montmorillonite

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1. Introduction

Electronically conducting polymers have been the subject of numerous investigations in the past two decades (Nalwa, 1997a; Novak et al., 1997; Miller et al., 1997; Skotheim et al., 1998). These materials have properties that make them suitable for several applications including light-emitting diodes, sensors, batteries, and electrochemical supercapacitors. For the majority of these studies, a single polymer was prepared by chemical or electrochemical oxidation of the corresponding monomer. This as grown oxidized polymer is not pure and can be actually considered as a composite since counterions are included in the polymer matrix as dopant. On the other hand, the formation of copolymer displaying electronic conductivity has been much less investigated (Gningue et al., 1988; Laborde et al., 1990; Peters et al., 1992; Talu et al., 1996; Nalwa, 1997b; Sanchez De Pinto et al., 1997; Cha, 1997; San et al., 1998; Khalkali, 2005; Yildiz et al., 2006). The main motivation for preparing copolymer composites lies in the possibility that these materials will display better properties and also to overcome the limitation of the rareness of new conjugated δ -bond-containing monomers.

The preparation of copolymers from a pair of monomers will lead to an increase of the number of conductive polymers obtained from the same set of monomers (San et al., 1998). However, the main drawback of PANI is the limited pH range in which PANI retains its electrochemical activity. This is to some extent a function of the counter ion balancing the positive charge of the protonated emeraldine base (Lindfors et al., 2004, 2008). But usually PANI becomes insulating and electrochemically inactive at pH above 4 (Diaz et al., 1980), which limits its use as a sensing platform for applications requiring neutral or alkaline electrolytes. Many approaches have been used to overcome this problem. These are based on (i) post-polymerization grafting of sulfonic groups onto PANI chains by fuming sulfuric acid treatment (Li et al., 2005), copolymerization of parent aniline with $-\text{COOH}$ or $-\text{SO}_3\text{H}$

functionalized aniline derivatives (Karyakin et al., 1994; Xu et al., 1997; Barbero et al., 2004; Benyoucef et al., 2010), or performing electropolymerization in the presence of various organic acids (Sun et al., 1998; Mu et al., 2002, 2003; Zhang et al., 2004, 2007; Barrios et al., 2006; Blomquist et al., 2009).

All these approaches, by introducing an ionogenic acidic group to the PANI structure, hinder the deprotonation of the conducting form of PANI (emeraldine) and thus extend its electroactivity toward less acidic pHs.

At the initial stages of the electrochemical polymerization, aniline is oxidized and becomes a radical cation, which leads to dimerization. The dimers of aniline, p-aminodiphenylamine (ADPA) as a dominant product along with benzidine and hydrazobenzene as minor products, are immediately oxidized and conjugated with aniline monomer. Polyaniline is formed on the electrode surface as a film by repeating this electrochemical process. However, the actual overall reaction seems to be more complicated, and the properties of the polymer formed by this method are changeable with the reaction conditions, such as applied potential, aniline concentration, pH, and electrode material.

With regard to polyaniline based copolymers, a pioneering work has been done by Borole et al. (2004) and Wei et al. (1989, 1990). They have reported that aniline could be copolymerized with o-toluidine to give rise to a copolymer film, of which conductivity could be controlled in a broad range. Copolymerization of aniline with N-butylaniline has been also reported (Bergeron et al., 1991). Copolymerization of aniline and o-toluidine by electrochemical and chemical method has been also studied (Dhawan et al., 1993). The resulting copolymer film found to have both good conductivity and solubility in common organic solvents. Lately, copolymerization of aniline with N-methylaniline (Langer et al., 1993) and that with 3-aminophenyl-boric acid (Porter et al., 1990) have also been documented and also the electrochemical copolymerization of aniline with o-aminobenzonitrile has been studied (Sato et al., 1994). These reports suggest that the copolymerization could provide us a convenient synthetic method to prepare new conducting materials with desired properties.

Here, we reported a preliminary spectroelectrochemical study of conducting polymers created using non-toxic cationic catalyst, known-as Maghnite- H^+ (Mag-H) (Yang et al., 1990; Belbachir et al., 2001). The polymerisation has been performed with aniline "polyaniline" and it has been extended to o-toluidine "poly(o-toluidine)" and copolymers of them. The properties of these polymers have been compared with those synthesized by bulk polymerisation. The relative reactivities are analyzed and the copolymers are characterized. The effect of the copolymer composition on polymer properties such as conductivity, UV-visible (UV-vis) and FT-IR spectroscopies, X-ray diffraction (XRD), Transmission electron micrographs (TEM), X-ray photoelectronic spectroscopy (XPS) and electrochemical response were evaluated.

2. Experimental

2.1 Materials

Aniline (from Aldrich) was distilled under vacuum prior to use and o-toluidine (from Aldrich) was used as received. Perchloric acid (from Merck) was suprapur quality and the water employed for the preparation of the solutions was obtained from an Elga Labwater Purelab Ultra system. A natural sodium montmorillonite clay (named as Maghnite) obtained from Tlemcen (Algeria) has been used

2.2 Catalyst structure

Various methods of analysis, such as ^{27}Al and ^{29}Si MAS NMR, show that Maghnite is a montmorillonite silicate. The elementary analysis of the selected samples obtained using X-Ray Fluorescence (XRF) is presented in Table 1. Acid treatment of Raw-Maghnite was indicated to cause a relative reduction in the content of octahedrally spaced Al_2O_3 and a relative increase in silica (SiO_2).

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	SO_3	PF*
Raw-Mag	69.39	14.67	1.16	0.30	1.07	0.50	0.79	0.16	0.91	11
Mag-H	71.70	14.03	0.71	0.28	0.80	0.21	0.77	0.15	0.34	11

Table 1. Elementary compositions of Protons exchanged samples "Maghnite" (Compositions wt%). PF* : Pert in Fire.

Table 2 shows the various types of montmorillonites studied, and it can be seen that Maghnite has 11.9 % more SiO_2 than Wyoming 19.35 and Montmorillon (Vienne, French) (Kerr et al., 1950; Damour et al., 1987). When treated with sulfuric acid, this difference is even greater; 14.21 % and 21.66 % as compared to Wyoming and Vienne Bentonite, respectively. Maghnite contains 5.60 % and 5.49 % less Al_2O_3 , than the Wyoming and Vienne clay, respectively.

Sample	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	Na_2O	K_2O	TiO_2	SO_3
Wyoming (USA)	50.04	20.16	0.68	00	1.46	0.23	Tr	1.27	00	00
Vienne (French)	57.49	20.27	2.92	0.19	0.23	3.13	1.32	0.28	0.12	00
Raw-Mag (Algeria)	69.39	14.67	1.16	00	0.30	1.07	0.5	0.79	0.16	0.91
Mag-H (Algeria)	71.70	14.03	0.71	00	0.28	0.80	0.21	0.77	0.15	0.34

Table 2. Composition in wt% of American, French and Maghnia Algerian montmorillonite.

Fig. 1. shows the X-ray diffraction patterns of Raw-Maghnite and Mag-H^+ . The basal spacing of the Raw-Maghnite was 15.02 Å. The titration of Raw-Maghnite with 0.25 H_2SO_4 resulted in the exchange of exchangeable cations for H^+ in the interlayer.

Damour et al. (1987), Kerr et al. (1950) and Kwon et al, (2001) reported that the decrease in the basal spacing indicates a loss of the interlayer water upon the replacement of Na^+ for H^+ . In particular, although the X-ray peak of the montmorillonite did not change substantially before or after the acid treatment, there was a decrease in the basal spacing. This implies that the original structure was well preserves after the acid treatment (Table 3).

The effects of the acid activation process on the FTIR spectrum of the treated Maghnite (Fig. 2) are summarised as follows: The intensity of the absorption band at 3630 cm^{-1} (Al-Al-OH coupled by Al-Mg-OH stretching vibrations) decreases with acid treatment. The bands at 3425 cm^{-1} and 3200 cm^{-1} (absorption of interlayer water) become more diffuse with acid treatment (Farmer, 1974). The intensity of the Si-O out of plane and Si-O-Si (2 bands) in plane stretching bands at 1116 , 1043 and 999 cm^{-1} have not been affected by acid treatment. The Al-Al-OH (920 cm^{-1}), $\text{AlFe}^{3+}\text{OH}$ (883 cm^{-1}) and Al-Mg-OH (846 cm^{-1}) deformation bands decrease with acid treatment. The intensity of the band at 796 cm^{-1} increases with treatment, reflects alterations in the amount of amorphous silica in accordance to the findings of others workers (Farmer 1979; Breen et al., 1995). The intensity of the band at 628 cm^{-1} (either Al-OH

or Si-O bending and/or Al-O stretching vibration) gradually decreases with acid treatment in good agreement with the findings by Komadel, (2003). The intensity of the band at 467 cm^{-1} (Si-O-Al and Si-O-Mg coupled by OH vibration or Si-O bending vibrations) is essentially unchanged.

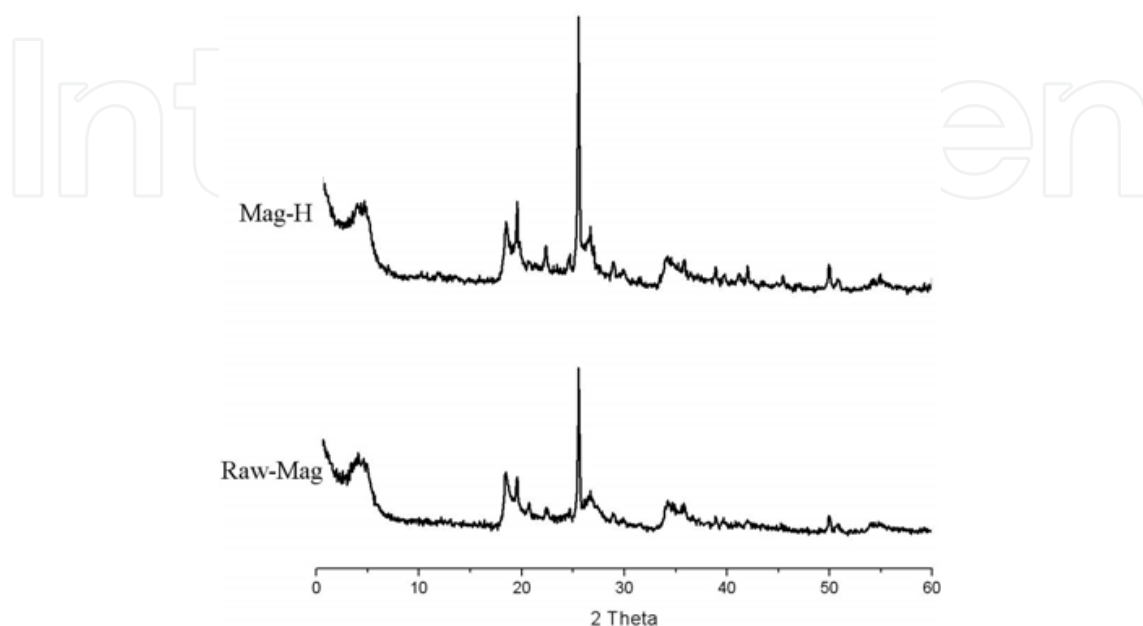


Fig. 1. X-ray Diffraction of Raw-Maghnite and Mag-H.

Samples	dhkl (\AA°)	Hkl	Nature of sample
Raw-Mag	12.50	001	Montmorillonite
	4.47	110	Montmorillonite
	4.16	//	Quartz
	3.35	//	Quartz
	3.21	//	Feldspath
	3.03	//	Calcite
	2.55	200	Montmorillonite
	1.68	009	Montmorillonite
	1.49	060	Montmorillonite
Mag-H	15.02	001	Montmorillonite
	4.47	110	Montmorillonite
	4.16	//	Quartz
	3.35	//	Quartz
	3.21	//	Feldspath
	3.03	//	Calcite
	2.55	200	Montmorillonite
	1.68	009	Montmorillonite
	1.49	060	Montmorillonite

Table 3. XRD characteristic of Raw-Maghnite and Mag-H.

^{27}Al NMR spectra of both Raw-Maghnite and Mag-H 0.25 M are given in Fig. 3. The spectra of Maghnite exhibits mainly the typical resonance at 2.9 ppm of octahedral aluminium (6Al) in a phyllosilicate but also a small but significant contributions at 60 and 68 ppm assigned to aluminium tetrahedrally co-ordinated to oxygen (4Al) (Samajová et al., 1992; Benharrats et al., 2003).

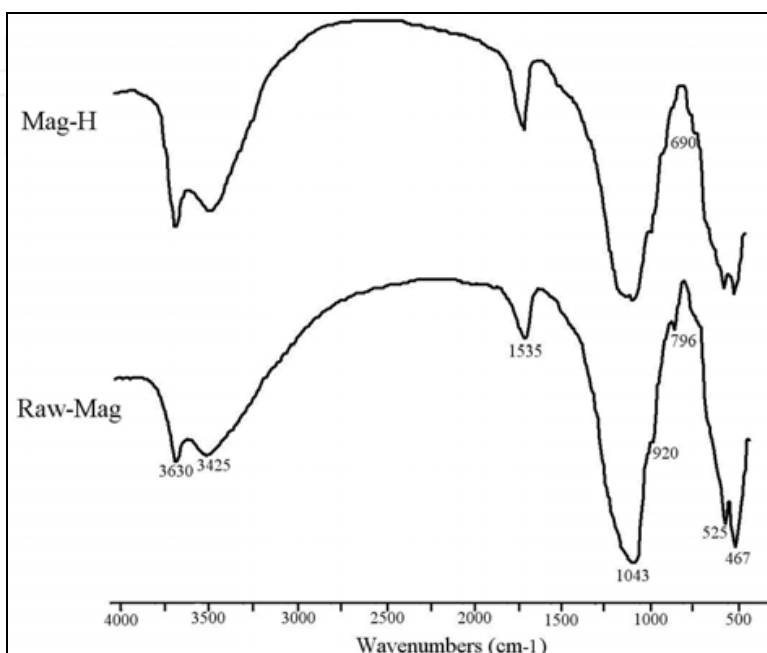


Fig. 2. IR Spectra of untreated Clay (Raw-Maghnite) and Acid treated Clay (Mag-H 0.25M).

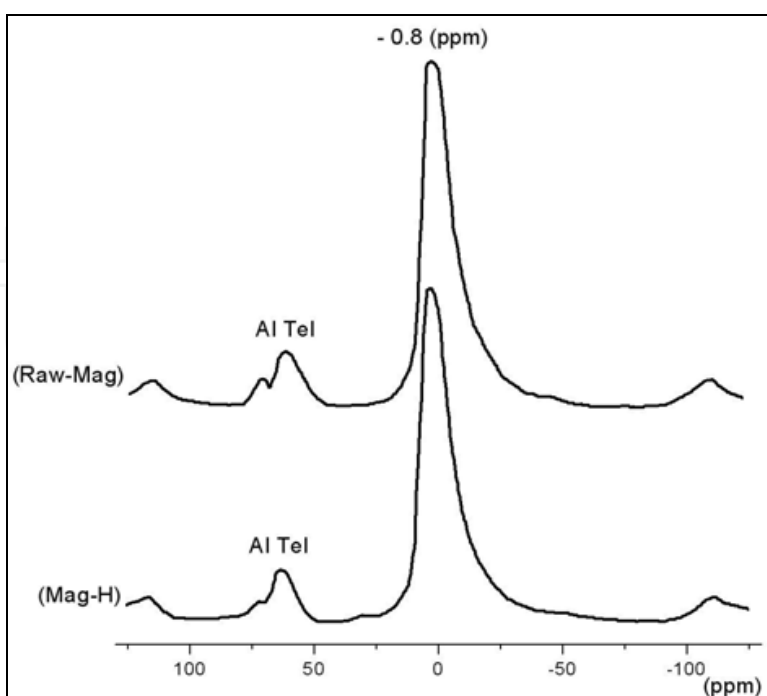


Fig. 3. ^{27}Al MAS NMR spectra of Raw-Maghnite and Mag-H.

The ^{29}Si MAS NMR spectra for the Raw-Maghnite and Mag-H 0.25M are shown in Fig. 4. The dominant resonance at -93.5 ppm corresponds to Q3 (O-Al) units, i.e. SiO_4 groups cross linked in the tetrahedral sheets with no aluminium in the neighbouring tetrahedral (Tkáč et al., 1994). The resonance at -112 ppm corresponds to three-dimensional (3D) silica with no aluminium present, designed Q4 (O-Al) (Tkáč et al., 1994; Kwon et al., 2001).

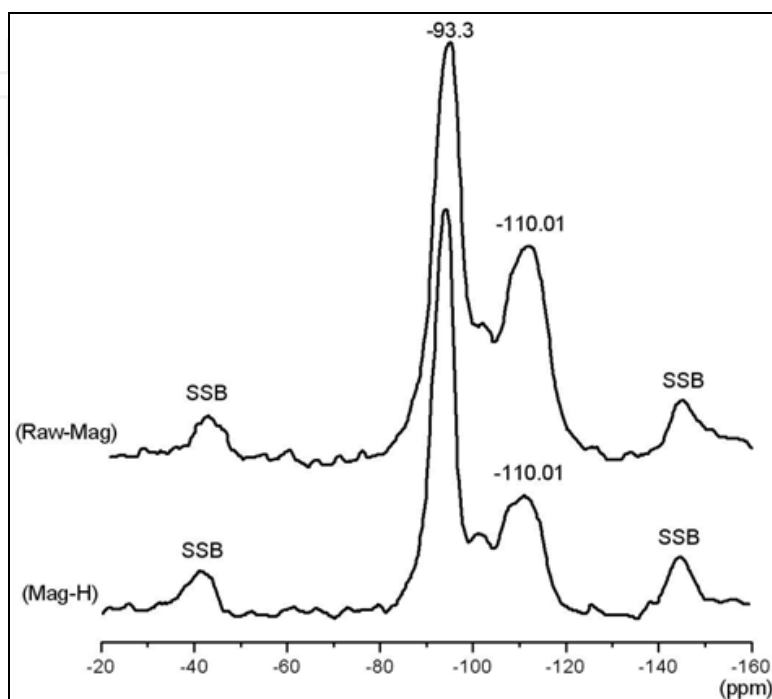


Fig. 4. ^{29}Si MAS NMR spectra of Raw-Maghnite and Mag-H.

2.3 Chemical synthesis

To obtain the polymer, 0.022 moles of monomers (aniline and/or o-toluidine) was added to 1 g of the clay and the mixture was kept under magnetic stirrer at room temperature for 1 hour. The chemical polymerization began when 100 ml of 0.1 M ammonium persulfate solution was slowly added to the mixture (thus, the final concentration of aniline and o-toluidine is 0.022 M). The reaction was carried out under magnetic stirring for 24 hours at room temperature and then the solid product was filtered under vacuum and washed with perchloric acid and distilled water to remove all traces of oxidant and oligomers. All the materials were dried at 60°C . The polymers remain into the catalyst layers forming a polymer at the last of the synthesis. However, the Mag-H is easy to separate by filtration because it is insoluble in the solvents in which the polymers are soluble (Njopwouo et al., 1988).

The same procedure was used for the copolymer synthesis, keeping always the mass ratio Mag-H/monomers (aniline and/or o-toluidine were added with molar ratios: 20/80, 50/50 and 80/20 to a total concentration of 0.22 M.) at 0.5.

2.4 Copolymer characterization

The X-ray diffraction of the powder nanocomposites were taken using a Bruker CCD-Apex equipment with a X-ray generator (Cu Ka and Ni filter) operated at 40 kV and 40 mA. X-ray fluorescence spectroscopy of the powder nanocomposites was made using a Philips PW1480

equipment with a UNIQUANT II software to determine elements in a semi quantitative way.

The XPS spectra were measured with a VG-Microtech Multilab electron spectrometer using non-monochromatised Mg K α (1253.6 eV) radiation from a twin anode source operated at 300W (20 mA, 15 kV). Photoelectrons were collected into a hemispherical analyser working in the constant energy mode at pass energy of 50 eV. The binding energy (BE) of the Cls peak at 286.4 eV was taken as internal standard. Peak analysis was done with mixed Gaussian/Lorentzian function lineshape by using the Peak-fit program implemented in the control software of the spectrometer. The pressure in the analysis chamber was always lower than 2.10^{-9} Torr. Thermal degradation of the samples does not occur because the time required to collect the XPS spectra is low.

The XPS measurements have been performed in the Mag-H/polymer samples. That is, the polymer has not been separated from the catalyst.

For recording the UV-Vis absorption spectra, a Hitachi U-3000 spectrophotometer was used. The solution of the copolymer in N-methyl-2-pyrrolidone (NMP) was used for recording the spectrum. Fourier transform infrared (FT-IR) spectroscopy was recorded using a Bruker Alpha.

For TEM experiments, the polymers were dispersed in water and then cast in TEM grids. The images were collected using a JEOL (JEM-2010) microscope, working at an operation voltage of 200 kV.

2.5 Conductivity

Conductivity measurements were carried out using a Lucas Lab resistivity equipment with four probes in-line. The samples were dried in vacuum during 24 h; and pellets of 13mm diameter were prepared using a FTIR mold by applying a pressure of 10 Tn/cm².

2.6 Electrochemistry

The electrochemical behaviour of the polymers was studied by cyclic voltammetry after their extraction from the composite by dissolving in the N-methyl-2-pyrrolidone (NMP). It is known that this kind of conducting polymers is soluble in NMP (Yoshimoto et al., 2004; Sung et al., 2005), while the clay remains in solid state. Thus, both components can be separated by filtration. The electrochemical measurements were carried out using a conventional cell of three electrodes. The counter and reference electrodes were a platinum foil and a hydrogen reversible electrode (RHE) immersed in the same electrolyte, respectively. The working electrode was prepared as follows: after the polymer was extracted from the polymer using NMP, 50 μ L of this solution were cast over graphite carbon electrodes and the solvent evaporated to create polymeric films. The electrolyte used was 1M HClO₄ and all experiments were carried out at 50 mV s⁻¹.

3. Results and discussion

3.1 Copolymer characterization

3.1.1 XRD

The Raw-Maghnite (Raw-Mag), the protonated Maghnite (Mag-H) and PoT/Mag-H nanocomposites were characterized using X-ray diffraction to check changes in the interlayer spacing (Fig. 5). The XRD patterns show that the (001) diffraction peak between 3.5° and 5.5° changes depending on the protonated and the polymer intercalated.

Table 4. includes the d-spacing between the montmorillonite sheets calculated from the Bragg equation, the basal spacing and the maximum 2θ of the peaks; that expressed by law :

$$n\lambda = 2d \sin\theta$$

where λ is the X-ray wavelength, d is the spacing between the atomic planes, and θ the angle between the X-ray beam and the atomic plane. Constructive interference occurs for integer values of n . By measuring θ for a known wavelength the Bragg spacing d can be determined.

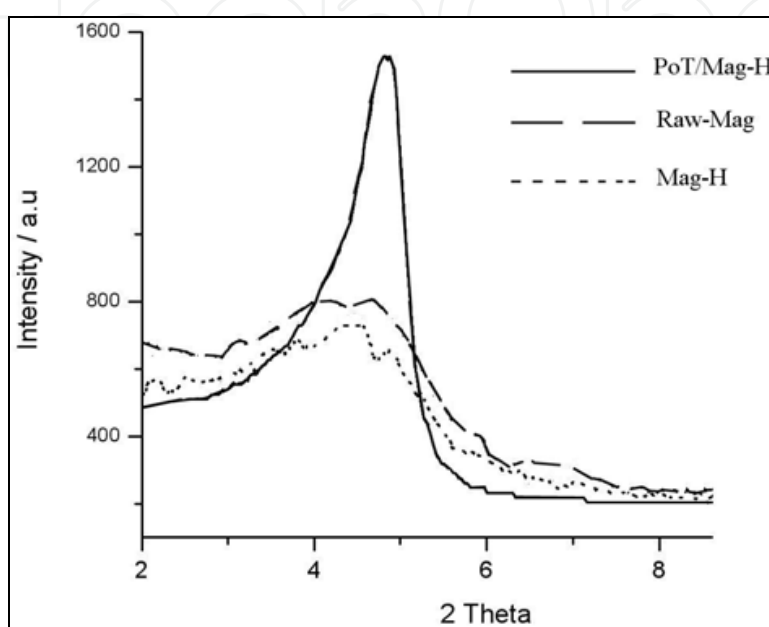


Fig. 5. XRD diffraction patterns of Raw-Maghnite and Protonated Maghnite (Mag-H) and PoT/Mag-H nanocomposite.

Polymers	Peak maximum, 2θ max (deg)	Basal spacing, $d_{(001)}$ (Å)	Interlayer spacing, Δd (Å)
Raw-Mag	4.5	13.4	3.5
Mag-H	4.4	13.2	3.3
PoT/Mag-H	4.9	14.1	4,6
P(Ani-co-oT)/Mag-H (20-80 ^a)	4.8	13.9	4.5
P(Ani-co-oT)/Mag-H (50-50 ^a)	4.9	13.9	4.5
P(Ani-co-oT)/Mag-H (80-20 ^a)	4.8	14.1	4.6

Table 4. Peak maximum and d-spacing of protonated and the nanocomposites intercalated into Raw-Maghnite. ^aFeed composition corresponding to aniline/o-toluidine ratio in the reactor.

3.1.2 XPS

Poly(o-toluidine), polyaniline and copolymer of them at different feed ratio (20/80, 50/50 and 80/20 aniline/o-toluidine ratio) were obtained using the procedure described in the experimental section and characterized by X-ray photoelectronic spectroscopy (XPS).

Fig. 6. shows the XPS spectra for poly(o-toluidine) synthesized using both the conventional and our method. The C1s signal for poly(o-toluidine) prepared using Mag-H (PoT/Mag-H) (Fig. 6a.) is practically identical to those obtained in perchloric acid (PoT/HClO₄) (Fig. 6b.). The C1s of poly(o-toluidine) can be deconvoluted into two peaks, the first one at 284.1 eV is assigned to aromatic carbons. The peak at 285.8 eV could be attributed to carbon atoms in quinonimine units and charged species (Chan et al., 1993; Belbachir et al., 2001) such as -C-N⁺ and -C=N⁺. However, this peak could correspond also to carbon atoms on the methyl group.

The N1s signal for both PoT/Mag-H (Fig. 6c.) and PoT/HClO₄ (Fig. 6d.) can be deconvoluted into two principal peaks attributed at both neutral amino or imine groups (399.2 eV) or positively-charged nitrogen atoms (402 eV). In Table 5, the ratio between charged and neutral nitrogen atoms (N⁺/N) increases remarkably when a small quantity of aniline is added to the feed. In polyaniline substituted with anionic groups, the N⁺/N ratio is related to either the doping level or the charge localization (Chan et al., 1993; Salavagione et al., 2004) however, the increase of N⁺/N in this case is only related to the increase in the doping level because the substituting group (-CH₃) is not an ionic species and therefore it is unable to fix charge.

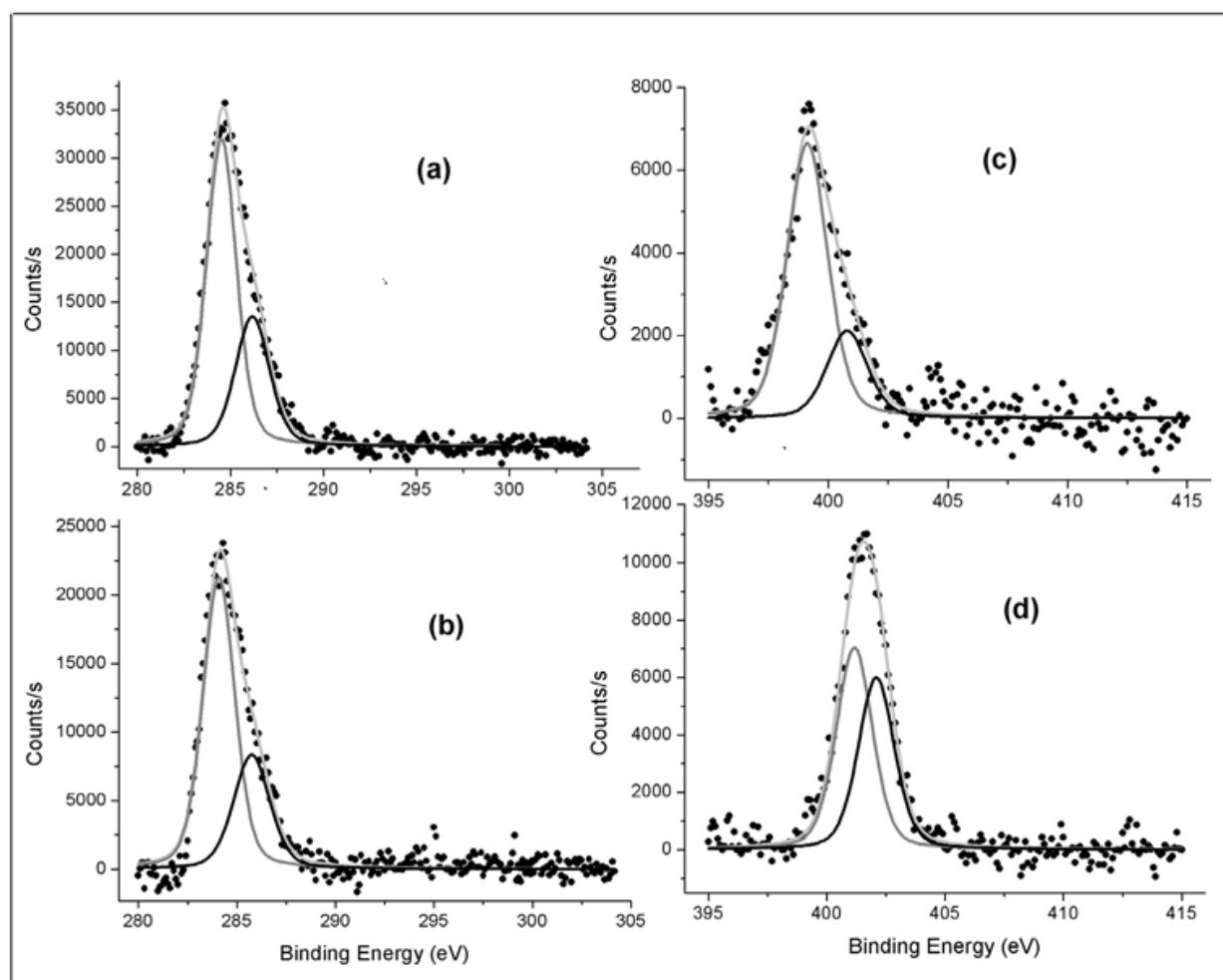


Fig. 6. XPS of poly(o-toluidine) for both C1s of PoT/Mag-H (a) and PoT/HClO₄ (b) and for N1s signal of PoT/Mag-H (c) and PoT/HClO₄ (d).

Table 5. shows the relative areas of the C1s peak for PoT and copolymers of aniline and o-toluidine at different feed ratio. Here, it can be noted that while the area of the peak at 284.1 eV decreases when the amount of o-toluidine in the feed increase (column C1/C in Table 5); however, the area of the peak at 285.8 eV increases (column C2/C in Table 5). Therefore, this signal at 285.8 eV has contribution of carbon linked to the methyl group and the peak at 284.1 eV only corresponds to carbon atoms in quinoneimine units.

Polymers	C1s Signal areas		N1s Signal areas
	C ₁ /C	C ₂ /C	N ⁺ /N
P(Ani-co-oT)/Mag-H (20-80 ^a)	0.626	0.374	0.486
P(Ani-co-oT)/Mag-H (50-50 ^a)	0.656	0.343	0.511
P(Ani-co-oT)/Mag-H (80-20 ^a)	0.684	0.315	0.666
PoT/MagH	0.673	0.327	0.320
PoT/HClO ₄	0.689	0.311	0.397

Table 5. Areas of the XPS signal of C1s and N1s for homopolymers of o-toluidine and copolymer of them. C refers to total carbons area, C1 refers to BE 284.1 eV and C2 correspond to 285.8 eV. ^aFeed composition corresponding to aniline/o-toluidine ratio in the reactor.

3.1.3 FT-IR spectroscopy

The FTIR spectra of homopolymers and copolymers are shown in Fig. 7. The spectral data of samples are in Table 6.

The FT-IR spectrum of PoT/Mag-H exhibits the following main spectral features (Kim et al., 1988; Gruger et al., 1994; Andrade et al., 1996) :

- i. The broadband at 1580 cm⁻¹ can be assigned to the C-C stretching mode combined with C=N stretching vibrations of the quinoid rings.
 - ii. The band at 1496 cm⁻¹ is attributed to the C-C stretching modes in the benzenoid units.
 - iii. The bands at 1325 cm⁻¹ and 1223 cm⁻¹ are assigned to the C-N stretching vibrations in the polymer chain.
 - iv. The band at 1158 cm⁻¹ is related to the C=N stretching mode; this band is a characteristic of doped PoT. It can be due to the doping of the PoT by the ambient gases.
 - v. The band at 1109 cm⁻¹ can be attributed to charge delocalization on the polymer backbone.
 - vi. The band located at 804 cm⁻¹ represents the paradisubstituted benzenoid rings in PoT.
- In addition, the presence of quinoid and benzenoid bands (1572 and 1515 cm⁻¹) shows that the PoT is composed of imine and amine units. As can be seen, the spectra for both polymers are almost identical and show most of the bands of very similar conducting polymers (Sariciftci et al., 1990).

Wavenumber (cm ⁻¹)		Band characteristics
PoT/HClO ₄	PoT/Mag-H	
579	582	C-H out of plane bending vibration
811	807	Paradisubstituted aromatic rings indicating polymer formation
878	871	Due to the methyl group attached to the phenyl ring
1109	1092	C-H in plane bending vibration
1160	1157	Vibration band of the dopant anion
1315	1325	Aromatic C-N stretching indicating secondary aromatic amine group
1496	1507	C-N stretching of benzenoid rings
1582	1578	C-N stretching of quinoid rings

Table 6. Characteristic frequencies of chemically synthesized poly(o-toluidine) synthesized with HClO₄ and with Mag-H.

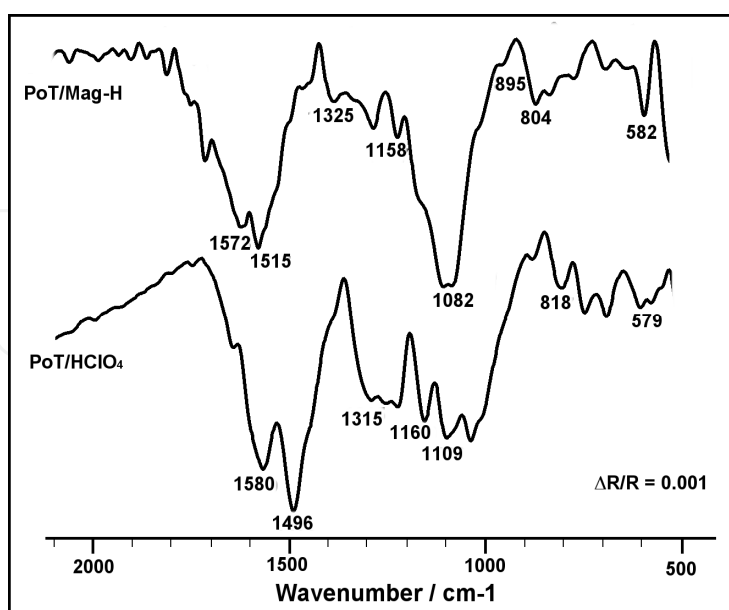


Fig. 7. FT-IR adsorption spectra of the of poly(o-toluidine) doped with Mag-H and with HClO₄.

The spectra of copolymer is shown in Fig. 8, they present features common to homopolymers synthesized using Mag-H. In the spectra of copolymer appears absorption band at 1109 cm^{-1} (C-H bending) and 1496 cm^{-1} (C-C stretching) indicating the existence of methyl group in the copolymer; besides this, new absorption band appears at 1109 cm^{-1} , which increases the intensity of the copolymer with increase of the o-toluidine content in the comonomer feed.

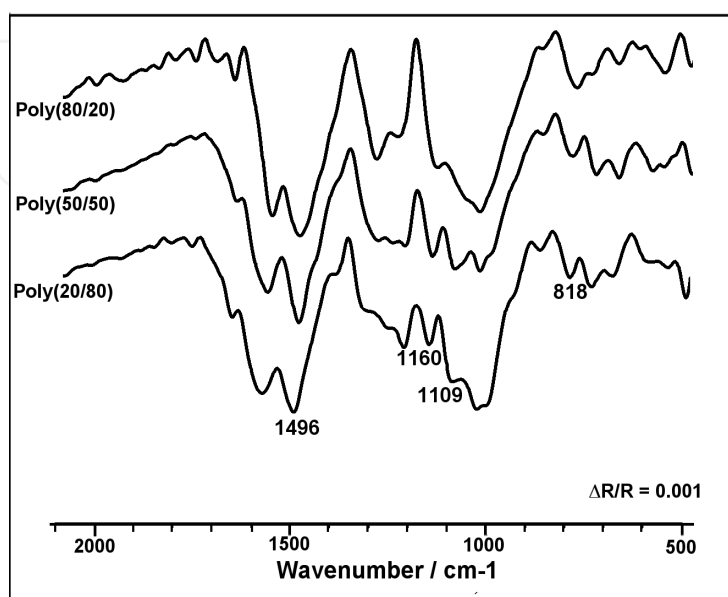


Fig. 8. FT-IR adsorption spectra of the copolymers with (aniline/o-toluidine) molar ratios (20/80, 50/50 and 80/20).

3.1.4 UV-Vis absorption measurement for the homo- and co-polymers

The absorption maxima for the PoT/Mag-H, PoT/HClO₄ and poly(ANI-co-oT)/Mag-H in DMSO solution are given in Table 7, it is observed that, there are two absorption bands in the electronic spectra of homopolymers and copolymers (Fig. 9). The band around 310 nm is assigned to $\pi-\pi^*$ which corresponds to band gap and the band above 600 nm is assigned to $n-\pi^*$ exciton band or inters band charge transfer associated with the excitation of benzenoid to quinoid rings (Chan et al., 1993; Yang et al., 2010).

Polymers	Bandgap Adsorption bands λ_{max} (nm)	Exciton Adsorption bands λ_{max} (nm)
P(Ani-co-oT)/Mag-H (20-80 ^a)	311	596
P(Ani-co-oT)/Mag-H (50-50 ^a)	316,5	599,5
P(Ani-co-oT)/Mag-H (80-20 ^a)	307,5	597
PoT/MagH	311,5	600,5
PoT/HClO ₄	309	600

Table 7. UV-Vis. absorption bands of polymers synthesized using Mag-H and HClO₄. ^aFeed composition corresponding to (aniline/o-toluidine) ratio in the reactor.

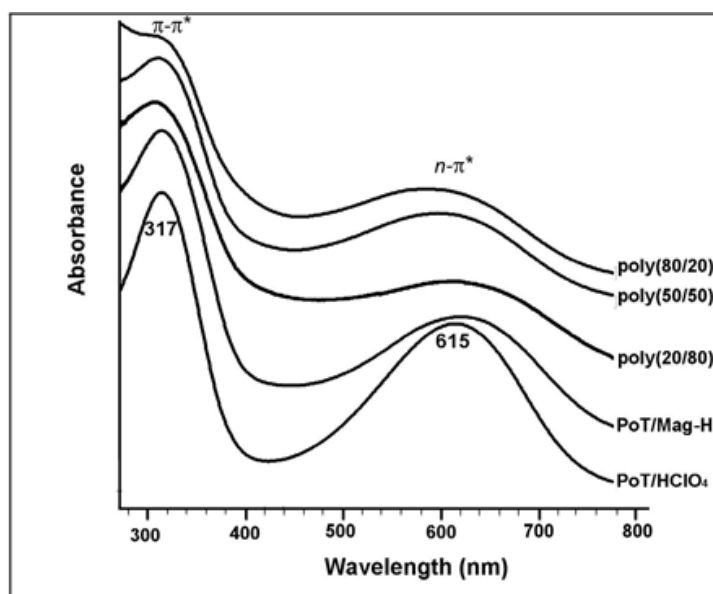


Fig. 9. UV-vis spectra of the poly(o-toluidine)/HClO₄ and poly(o-toluidine)/Mag-H.

The $\pi-\pi^*$ transition of copolymers shows hypsochromic shift (blue shift). This may be due to the increase the degree of freedom and entropy of solvation. The $n-\pi^*$ exciton band shows a bathochromic shift (red shift) with an increase in dielectric constant of the solvent (Kim et al., 1988). The $\pi-\pi^*$ band in copolymer shifts to the lower wavelength (higher energy) as the mole percent of o-toluidine in copolymer increases, which may be due to addition of more o-toluidine unit, which twist the torsion angle, which is expected to increase the average bandgap in conjugated polymer chain.

3.2 Copolymer properties

3.2.1 Conductivity

The conductivities of homopolymers and copolymers are given in Table 8. The values lie in between 2.19×10^{-5} and 2.24×10^{-3} S.cm⁻¹. The conductivity of chemically synthesized PoT/HClO₄ salt show very low conductivity (2.02×10^{-3} S.cm⁻¹) is higher than that of PoT/Mag-H salt (2.19×10^{-5} S.cm⁻¹).

Polymers	Conductivity (S.cm ⁻¹)
P(Ani-co-oT)/Mag-H (20-80 ^a)	2.24×10^{-3}
P(Ani-co-oT)/Mag-H (50-50 ^a)	1.52×10^{-4}
P(Ani-co-oT)/Mag-H (80-20 ^a)	6.26×10^{-5}
PoT/MagH	2.19×10^{-5}
PoT/HClO ₄	2.08×10^{-3}

Table 8. The conductivity values of polymers synthesized with HClO₄ and Mag-H. ^aFeed composition corresponding to (aniline/o-toluidine) ratio in the reactor.

The conductivity of all the copolymers was found to be higher than that of the homopolymers PoT/Mag-H ($2.19 \times 10^{-5} \text{ S.cm}^{-1}$). The conductivity increases with aniline content. The higher conductivity of the copolymers compared to that of the PoT/Mag-H homopolymers indicates lowering of the band gap in the copolymers formed with toluidine (with a donor $-\text{CH}_3$ group). This finding is supported by the bathochromic shift of the peak around 600 nm in the electronic absorption spectra of the copolymers as discussed later. However, the steric effect of the methyl group is likely to disrupt the overlapping of orbitals, hence lowering the degree of conjugation, by forcing the aromatic rings out of plane relative to each other. The poorer polaron formation of the copolymers with the higher concentration of o-toluidine is consistent with the conductivity decrease of copolymers. These results are reasonable because the self-doping degree must decrease as the aniline mole fraction increases. Therefore, we can conclude that all copolymers have some degree of self-doping despite the lower reactivity of o-toluidine monomer.

Also it is also possible that the addition of aniline in the ratio of copolymers curing affects the chain alignment of the polymer, which leads to the increase of conjugation length and that brings about the increase of conductivity.

3.2.2 Solubility

The solubility of PoT/Mag-H, PoT/HClO₄ and these copolymers of aniline/o-toluidine in different solvents are shown in Table 9. The solubility decreases with increasing the concentration of aniline units in the copolymer. The solubility improvement of polymers prepared with Mag-H compared with HClO₄ must be related to the presence of anionic and/or cationic groups (from the natural sodium montmorillonite clay units) in the synthesis of polymers.

Samples	NH ₄ O H	DMSO	THF	NMP	Etha -nol	CH ₃ C OOH	Tolue -ne	Acet -one	CCl ₄	C ₆ H ₆
P(Ani-co- oT)/Mag-H (20-80 ^a)	S/BV	PS/BR	PS/ BG	PS/ BR	IS	PS/B	PS/ BG	IS/ BR	IS	IS
P(Ani-co- oT)/Mag-H (50-50 ^a)	S/BV	S/BV	PS/ BR	S/BR	PS/ BV	PS/ BG	IS	PS/ BR	IS	IS
P(Ani-co- oT)/Mag-H (80-20 ^a)	S/V	S/BV	S/ BR	S/BV	PS/B	S/V	IS	PS/ BR	PS/ B	IS
PoT/MagH	S/V	S/BV	S/ BV	S/BV	PS/ BV	S/V	IS	PS/ BR	PS/ B	IS
PoT/HClO ₄	S/V	S/BR	S/B R	S/BR	PS/ RC	PS/B	IS	PS/ V	IS	IS

Table 9. Solubility of PoT/Mag-H, PoT/HClO₄ and copolymers (Aniline/o-Toluidine) in different solvents. Solubility in solvents (IS = Insoluble ; PS = Partially ; S : Soluble). The solution color is indicated in the parentheses with the following abbreviations (V : Violet ; BV : Bluish violet ; BR : Brownish red ; BG : Bluish green ; B : Blue).

The solubility of the resulting conducting polymer of (Aniline/o-Toluidine) increases with increasing the feed ratio of o-toluidine in the polymerization, and it was observed that the highest solubility gives a low conductivity. That is to say when the solubility decreases the

conductivity increases. This result indicates the solubility of polymers synthesized with Mag-H decreased with increasing polymer chain.

3.2.3 Electrochemical response

To study the electrochemical response of polymers and copolymers, a conventional cell of three electrodes was used. To separate the polymers from the catalysts, they were dissolved in N-methyl-2-pyrrolidone (NMP). Films of the polymers were made by casting a drop of a solution of them in NMP over the electrode and heating with an infrared lamp to remove the solvent.

Fig. 10. shows the voltammograms obtained with the two electroactive poly(o-toluidine) films in 1M HClO₄ solution. The current densities have been normalized in order to clearly compare between the two polymers, due to the thickness of the films could vary from different samples. The electrochemical behaviour of the PoT/Mag-H exhibits two anodic peak around 0.48V and 0.71V however, on the reverse scan two reduction peaks around 0.59 V and 0.40 V are observed. This behaviour differs from those obtained when the polymer is created in acidic conditions (PoT/HClO₄, Fig. 10. continuous line). The polymer created in HClO₄ shows the similar electrochemical response reported by Borole et al. (2003, 2004, 2006), two pairs of redox peaks were detected with a potential shift at 0.58/0.37V and 0.73/0.65V.

To try to clarify all peaks observed, we have synthesized polyaniline and copolymer of aniline/o-toluidine with Mag-H as proton source. The cyclic voltammogram of these copolymers obtained by Mag-H is shown in Fig. 11. The voltammetric behaviour of copolymer (aniline/o-toluidine) (20/80) is similar to those obtained in PoT/Mag-H. At higher concentration of aniline monomers (50/50), two pairs of anodic and cathodic current peaks are seen clearly, centred at around 0.51 and 0.80V. At lower electrode potentials, not exceeding 0.51V, the reduced (leucoemeraldine) form prevails, whereas at high potentials, exceeding ca. 0.80V, the fully oxidized (pernigraniline) form exists, leaving a broad potential window, ranging from 0.51 to 0.80 V, where the conducting emeraldine form is most stable. In addition, for copolymers with high amounts of aniline (80/20) shows the same behaviour (two redox process). Therefore, besides that the properties of this kind of conducting polymers do not depend on the type of anion used in the synthesis (Chan 1993), the electrochemical properties depend strongly on the proton source (inorganic acids or Mag-H catalyst).

3.2.4 TEM

Fig. 12. show the transmission electron micrographs of two typical polymers PoT/Mag-H and PoT/HClO₄. Transmission electron micrographs of the PoT/Mag-H reveal a structure similar to those of PoT/HClO₄. Presence of chopped fibers in the two polymers can be explained by considering the steric contribution of the methyl group. The methyl group present at the ortho position of the benzene ring leads to a distortion in the polymer chains and restrict the polymer growth in a linear fashion, which in turn results in a breakdown of the polymer chain into small fragments and this appears as small chopped or needle shaped fibers in the micrograph. Interestingly the polymer of PoT/Mag-H is more chopped fibers comprising of a whole polymer matrix than the corresponding PoT/HClO₄. The interplanar distances, however, do not exhibit any perceptible change with the two different methods of synthesis. The PoT/Mag-H apparently has larger interplanar distances than the corresponding PoT/HClO₄.

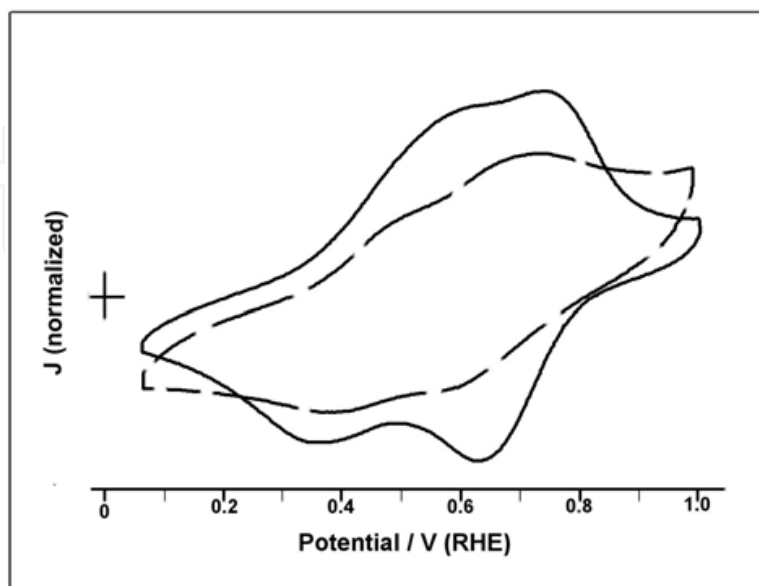


Fig. 10. Cyclic voltammograms recorded for a graphite electrode covered by PoT/Mag-H (dashed line) and PoT/HClO₄ (solid line) in 1M HClO₄ solution. Scan rate 50 mV s⁻¹.

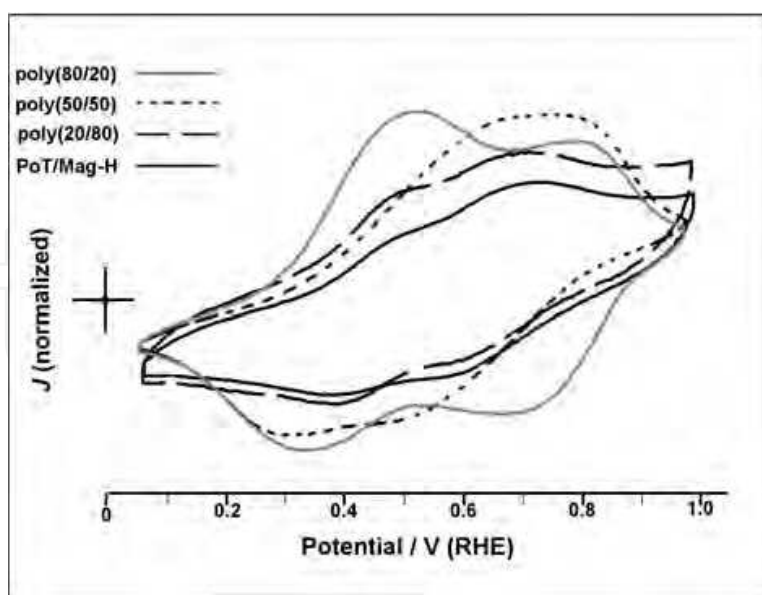


Fig. 11. Cyclic voltammograms recorded for a graphite carbon electrode covered by copolymers the feed ratio (20/80, 50/50 and 80/20 aniline/o-toluidine ratio) in 1M HClO₄ solution. Scan rate 50 mV s⁻¹.

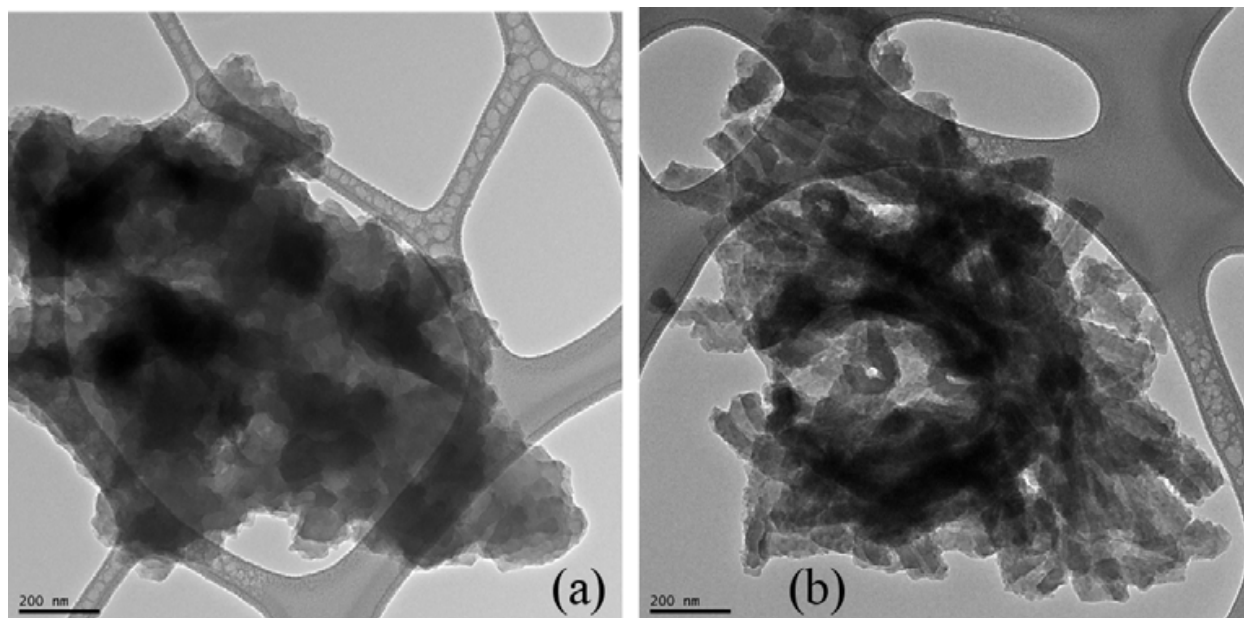


Fig. 12. Transmission electron micrographs (TEM) of poly(*o*-toluidine) doped with HClO_4 (PoT/ HClO_4) (a) and doped with Mag-H (PoT/Mag-H) (b).

4. Conclusions

We have developed a new synthetic method to produce conducting polymers, which does not use inorganic acid but a non-toxic clay catalyst as proton source. Preliminary results about the spectroelectrochemical properties have been shown. However, we can conclude that the electrochemical behaviour of PoT/Mag-H is quite different from those observed for PoT/ HClO_4 . The polymers synthesized using Mag-H could show a structure that is a mixture of conducting (polyaniline-type) and redox (phenazine-type) units.

The degree of d-spacing of PoT/Mag-H nanocomposites was expanded to 4.6 (\AA) compared to the Mag-H 3,3 (\AA), this result shows the strong interaction between PoT and Mag-H that gives additional stability to the intercalated polymer within the matrix. The nanocomposite is having good conductivity, but less than that of pure PoT, due to the weakening in interchain interactions within the confined matrix. In addition, the PoT/Mag-H is more soluble in different solvents than PoT/ HClO_4 .

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