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Maghnite-H+, An Eco-catalyst layered (Algerian Montmorillonite) for Synthesis of Polyaniline/Maghnite Nanocomposites

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Abstract

The nanocomposites namely Polyaniline/Maghnite clay (PANI-Mag) composites were synthesized by solution polymerization of aniline in the presence of sulfuric acid and amount of potassium persulfate (PPS), with molar ratio of monomer to oxidant of 2:1, the aniline was polymerized and largely incorporated into the Maghnite,which was confirmed by FTIR ,HNMR spectra and UV-Vis spectroscopy shows some peaks shifts, which indicate the formation of some new bonds and support the intercalation of PANI chains into the interlayer spacing of Maghnite MMT clay. That, the morphology of the PANI-Mag composites changed according to the proportion of clay. The conductive emeraldine salt form of polyaniline PANI-ES is inserted into the layers of maghnite clay to produce the hybrid with high conductivity and solubility in various organic solvents. The resulting organic-inorganic hybrid material, PANI-Mag has been characterized by various physicochemical techniques**.**

Keywords: PANI-ES , GPC , Nanocomposite , Maghnite , H-NMR , Emeraldine base ,Kenetics studies , polymers conductors.

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1 Introduction

For commercial applications, PAN is the best promising material in conducting polymers, because of environmental stability [1], easy processing [2], and economical efficiency [3]. PAN has been used for electrode of light emitting diode [4], Li ion rechargeable battery [5] and corrosion protection [6].Among organic-inorganic nano-composite-sites, PANI-Mag nanocomposites are the most prevalent and interesting due to the special properties as well as wide uses of polyaniline [7], the nature, abundance, low cost of Mag and attractive features such as a large surface area and ion-exchange properties [8].

Clay minerals especially the members of smectite group are the most suitable candidates for synthesis of polymer nano-composites, because these possess a unique structure and reactivity together with high strength. In general, the structures of polymer/clay nanocomposites are classified according to the level of intercalation and exfoliation of polymer chains into the clay galleries [9]. Various parameters including clay nature, organic modifier, and polymer matrix and preparation method are affective on the intercalation and exfoliation level. Therefore depending on the nature and properties of clay and polymer as well as preparation methodology of nanocomposites, different composite micro-structures can be obtained [10].

The series of nanocomposites namely Polyaniline/Maghnite clay (PANI-Mag) were synthesized by solution polymerization of aniline in the presence of sulphuric acid and amount of potassium persulfate (PPS), with molar ratio of monomer to oxidant of 2:1, the aniline was polymerized and largely incorporated into the Mag, which was confirmed by FTIR ,1H-NMR spectra and UV-Vis spectroscopy shows some peaks shifts, which indicate the formation of some new bonds and support the intercalation of PANI chains into the interlayer spacing of Maghnite(Mag-H+) clay[11].

2 Experimental section

2.1 Materials

Aniline 99%, potassium persulphate 98% (Aldrich) , hydrochloric acid (35%–38%),MMT clay was obtained from ENOF Maghnia (Algeria). The MMT-H^+ (Mag-H^+) was prepared as described by Belbachir and al [12], and water (PH<7) were used to synthesis emeraldine salt (PANI-Mag-H^+) by emulsion polymerization. Some of the emeraldine base (PANI-EB), non-conducting form of polyaniline, was prepared by de-protonating PANI-ES in NaOH Solution (0, 5 M). A doping EB was carried out in aqueous medium of hydrochloric acid (HCl) [13].

2.2 Preparation of catalyst (Maghnite-H^+)

Maghnite-H^+ was prepared according to the process reported in our previous study [14]. Raw-Maghnite (20 g) was crushed for 20 mn using a prolabo ceramic balls grinder. It was then dried for 2 h at 105ºc. The Maghnite was placed in an Erlenmeyer flask together with 500 ml of distilled water. The Maghnite/water mixture was stirred using a magnetic stirrer and combined with 0.25 M sulfuric acid solution, until neutralization was achieved over 2 days at room temperature, the mineral was then washed with distilled water to become sulfate free and then dried at 105º C .

2.3 Procedures of synthesis

The present study provide process for preparing polyaniline or another polymer conductors such as (polypyrole , plythiophene) or substituted polyaniline (o-anisidine , o-methoxy-aniline , o-toluidine …….) , which comprises dissolving oxidizing agent (solid) slowly in mixture of catalyst and monomer (Mag-H^+ , aniline) after 30 mn at ranging temperature (0ºC to 4ºC) and during 10 mn , after this time we added drop by drop 15 ml to 20 ml of water , the reaction mixture was stirred for 1h 30 mn at the optimal conditions . At the end of polymerization, we obtained the polyaniline /clay nanocomposites (PANI- Mag-H^+). Eventually, the result it's black solution (polymer-solvent) , after evaporation result a black powder it's (PANI-Mag),washed several times with water and methanol , where dried at 60ºc for 48 h for characterization .

2.4 Polymer characterization

Measurements of 1H NMR spectra were conducted in D2O solution, under ambient temperature on an AM 300 FT Bruker spectrometer using tetramethylsilane (TMS) as internal standard. IR absorption spectrum was recorded on an ATI Matson FTIR No 9501165 spectrometer using the KBr pressed disc technique. Gel permeation chromatography (GPC) was performed with a Spectra-Physics chromatograph, equipped with four columns connected in series and packed with Ultrastyragel 103, 104, 105, 106 Å. Tetrahydrofuran (THF) was used as solvent and the instrument was calibrated to a first approximation with polystyrene of known molecular weights. Viscosity measurements were carried out with an Ubbelohde capillary viscosimeter (viscologic TI1, version 3-1 Semantec). Intrinsic viscosity, [η] (ml/g), was measured at 25°C in THF.

3 Results and discussion

Montmorillonites have both Bronsted and Lewis acid sites and when exchanged with cations having a high charge density, as protons, produce highly active catalysts for acid-catalysed reactions [15]. It have been demonstrated that intercalated organic molecules on the surface of Montmorillonite are mobile and can be highly polarize when situated in the space between the charged clay layers [16 ,17]. The present study examines the catalytic activity of Algerian proton exchanged montmorillonite clay (Maghnite-H^+). It was demonstrated that there is an excellent correlation between the acid treatment and the catalytic activity of Maghnite [18].

3.1 FTIR Spectra of catalyst (Mag–H^+)

FTIR spectra have been widely used to characterize the polymer–clay nanocomposites [19] and are also used in this work. The FTIR spectra in fig.1 show the presence of characteristic peaks of Maghnite from the extracted nanocomposites. In addition, absorption bands related to silicate are also found, such as OH stretching of lattice water (3630 cm−1), H–O–H bending (1635cm^{-1}), Si–O–Si stretching (1043 cm−1), and Si–O stretching and Si–O bending (600–400 cm−1).

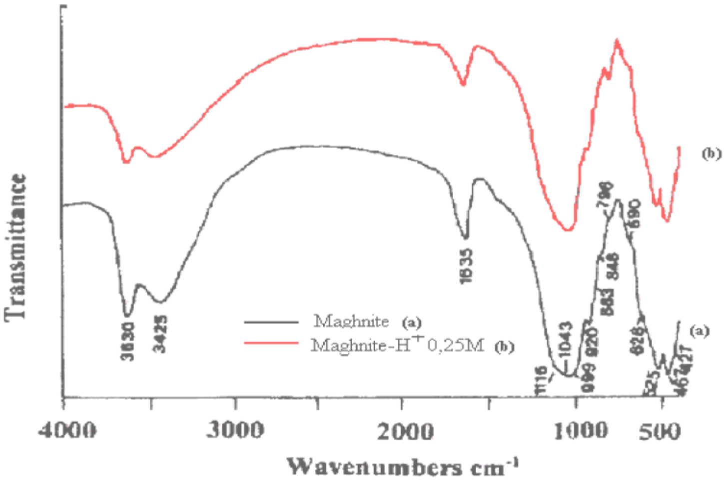

Fig 1: Infra red specra of raw maghnite and maghnite actived 0,25 M.

3.2 FTIR Spectra of nanocomposite PANI–Mag

The formation of polyaniline–Mag nanocomposites is confirmed from the infrared spectroscopy shown in fig.2. The FTIR spectra of the products show the characteristic

vibration of polyaniline, which agrees well with that of chemically synthesized polyaniline. They exhibit all the bands observed for polyaniline and the swollen Maghnite. In addition, for polyaniline, the literature data indicated that the characteristic absorption peaks are assigned to the C–H aspect bending vibration on the replaced benzene ring at 838cm^{-1} and the C–N bond stretching vibrations at 1293 cm^{-1}. 1501 and 1557 cm^{-1} represent the absorption peaks of benzene- and quinine-type in polyaniline chain.

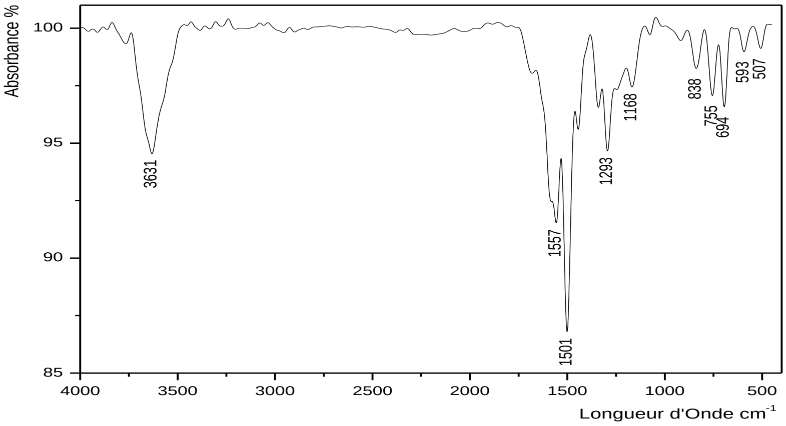

Fig 2: FT-IR spectra of the polymer (PANI-Mag) obtained by the intercaled method between Aniline and Maghnite (black powder) at 0°C.

3.3 H-NMR Spectra of nanocomposite PANI–Mag

The 1H-NMR spectra of the PANI-ES and PANI-EB polymers exhibit strongest sharp peak centered at 7 ppm and 7,8 ppm due to protons on phenylene and disubstituted phenylene units, the weak peak at 4.81 ppm and medium broad peak at 6.22 ppm due to (–NH– and –NH2) end group respectively, another broad peaks centered at 1,78 ppm and 8 ppm may be due to the water protons bonded by (–NH– and –NH2) groups and (H-N+) respectively, as show in Fig.3 [10] .

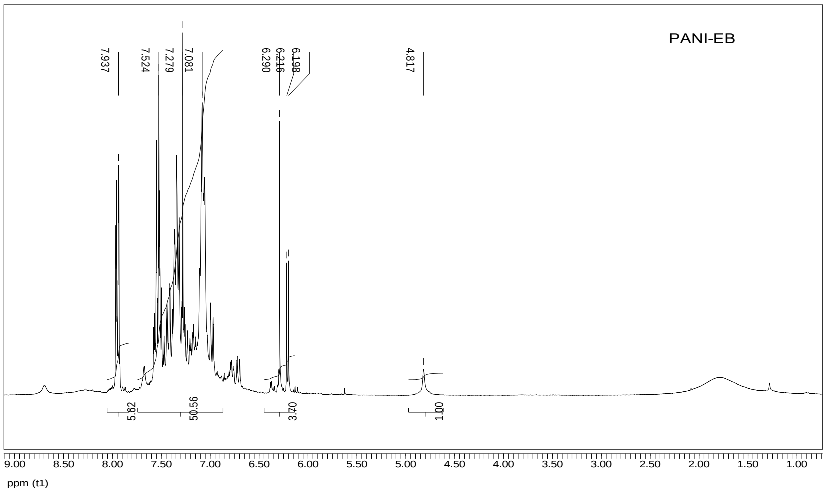

Fig 3: 1H NMR spectrum (300 MHz, CDCl3, Tetramethylsilane (TMS) was used as the internal standard) of polyaniline-Maghnite (PANI-EB-Mag) obtained by the polymerization of aniline with Mag-H+ initiator system in CDCl3 at 0°C.

3.4 Optical characterization

Polyaniline nanocomposite result of the oxidation of aniline in montmorillonite (maghnite) is demonstrated by the UV spectra. The spectra exhibit typical PANI-ES, including the transition from the black color of protonated PANI-ES in maghnite to black dark color corresponding to PANI-EB in alkaline ones. The UV-visible spectrum of PANI solution in chloroform has three absorption peaks 300 nm, 400 nm and 565 nm. It should be mentioned, however, that the absorption maxima are black by about 1hour compared with the PANI-MMT spectra reported in the literature [11]. This especially applies to PANI-EB, where absorption maximum of dispersions in *N*-methyle-2-pyrrolidone solutions were located typically at 610 and 635 nm, respectively [12]. Based on the UV spectra, we now know that polymer chains have different electronic structures in chloroform and *N*-methyle-2-pyrrolidone. This difference in electronic structures can be attributed only to their difference in conformational structures. Specifically, polymer chains of PANI have a more extended conformation and hence a longer conjugation length in *N*-methyle-2-pyrrolidone than in chloroform.

3.5 Results of GPC

Gel permeation chromatography (GPC) was performed with a Spectra-Physics chromatograph, equipped with four columns connected in series and packed with Ultrastyragel 10^3, 10^4, 10^5, 10^6A° , tetrahydrofuran (THF) was used as solvent and the instrument was calibrated to a first approximation with polystyrene of known molecular weights. The GPC curves for PANI indicate a bimodal distribution. The molecular weight distribution averages for the polymer are presented in Table.1 and Fig 4.This bimodal distribution has been reported previously for PANI in N-methyle-2-pyrrolidone.The molecular weight of the polymer shows the growth of PANI on PAN-Maghnite. Several reactions were done for many summers to follow the influence of physicals chemicals properties on the molecular weight of polymer.The yield of polymerization and the molecular weight of polyaniline were determined in dependence on the ratio of aniline, amount of catalyst, temperature, reaction time and a volume of water added. It was found that polymerization yield and molecular weight decrease with the increasing ratio catalyst to aniline, water and temperature. This result shows the cationic nature of the mechanism put into play results .Similar have been observed with other polymerization reactions catalyzed by Maghnite-H + [13-14].

Table 1: GPC of PANI-ES composite in THF

	Sample Name	RT	Area	% Area	Mn	Mw	Polydispersity
1	PANI-ES	17.973	1318425	6.01	644	746	1.158385
2	PANI-ES	23.638	20616395	93.99	33	114	3.413146

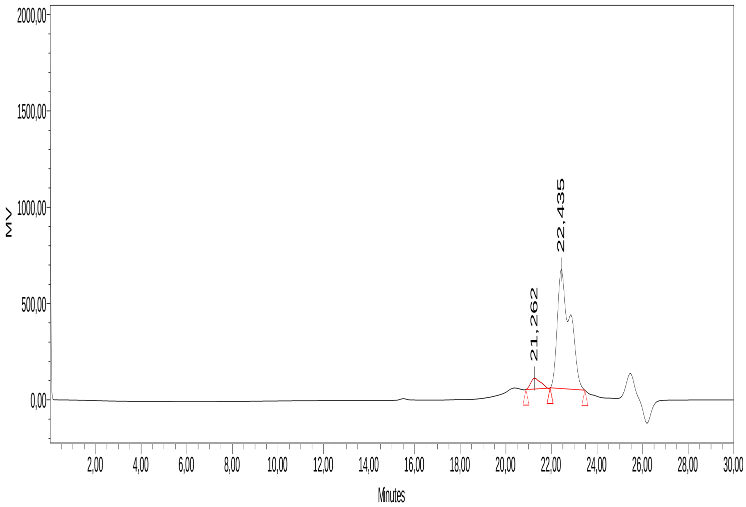

Fig.4. GPC chromatogram of PANI-ES with 6% Mag-H at 0°C for 1 h30 mn ; Number-average molecular weight = 644 g/mol, weight-average molecular weight=746 g/mol, and Polydispersity=1.15.

3.6 Thermodinamics properties

Completely soluble polyaniline-Maghnite clay (Mag–PANI) composite with drastically enhanced conductivity, improved thermal stability, and solubility, has been synthesized. Here, polyaniline exists in its soluble non-conducting and conducting form as shown in Table 2.

Table 2: Thermodynamics properties of different forms of polyaniline-Mag T (°C), ΔH (J/g), ΔCp (J/g*°C)

Sample	T_1	T_2	T_3	Tg	ΔH_1	ΔH_2	ΔH_3	ΔCp
PANI-EB-Mag	55.99	103.46	X	74.06	4.3161	20.5363	X	0.311
PANI-ES-Mag	50.34	140.10	221.07	103.75	167.6042	4.4617	10.7719	0.154
PANI-HCl-Mag	100.45	163.09	218.57	126.89	1.9678	8.7614	16.8337	0.180

3.7 Kenetics studies of the reaction

3.7.1 Effect of the amount of Mag-H+ on the polymerization

The effect of the amount of Maghnite-H+ on the yield of polymerization was examined (Table 3). It can be noted that the yield increases with increasing “Maghnite- H+ 0.25 M” proportion polymerization was carried in bulk at 0 °C. The polymerization rate increases with the amount of Mag-H+, In contrast, the intrinsic viscosity (η) is inversely proportional to the amount of Mag-H+, in which the effect of Mag-H+ as a catalyst is clearly shown. This phenomena is probably the result of number of “initiating active sites” responsible of inducing polymerization, this number is prorata to the catalyst amount used in reaction. Similar results are obtained by Belbachir. Indeed, using various amounts of Mag-H+, 2, 4, 6,8 and 10 % by weight, the and al [15-16].

Table 3: Effect of the catalyst (Mag-H^+) on the yield of polymerization.

Maghnite-H^+ 0.25M (%)	Yield (%)	η (dl/g)
2	49.12	1.85
4	59.61	1.68
6	66.94	1.49
8	75.86	1.07
10	84.03	0.98

3.7.2. Effect of the temperature on the polymerization

Table.4. shows the experimental results for the polymerization of Aniline (0,022 mol) with induced by (6% of Maghnite- H^+ 0.25 M) proceed in bulk at different temperatures. It was found that Maghnite- H+ by itself possesses good activity as catalyst for the polymerization. The yield of polymerization and the intrinsic viscosity reach maximum values around 0-5°C. On the other hand, with the increase in the reaction temperature above 5°C the intrinsic viscosity and the yield of the obtained polymers decrease progressively suggesting the possible occurrence of thermal degradation [17-18].

Table 4: Effect of reaction temperature on the yield of polymerization.
[Aniline]=0.022mol/l ; 6% of Maghnite-H+ ; Reaction time 3h ; determined in $CDCl_3$ at 25°C.

T (°C)	Yield(%)	η (dl/g)
0	80.53	1.32
5	76.45	1.21
10	50.19	0.95
20	42.02	0.83
30	33.27	0.57
40	25.11	0.30

3.8 Conductivity measurements

Method for measuring the electrical conductivity by the four-point method. Four points aligned and spaced the same distance are applied by simple pressure on the sample. A current I is injected through the outer tips with a current source, thus creating a potential variation. Voltage U can be measured between two points connected to internal voltmeter[19-20].

1) $\rho = R (\pi . r^2 / e)$ (Ω.cm)
2) $\sigma = 1/ \rho$ (S/cm)

The measured value of the transverse strength of the polyaniline is converted to volume resistivity, using equation (1), and then the electrical conductivity is calculated from the equation (2). In applying these equations, the value of (σ) presented in the following table5:

Table 5: Results of measuring the conductivity of different forms of polyaniline

sample	e(cm)	R(Ω)	ρ(Ω. Cm)	σ(S/cm)
PANI-ES-Mag	0.1	0.609	0.584	1.712
PANI-EB-Mag	0.1	1.880	25.792	0.038
PANI-HCl-Mag	0.1	0.976	0.163	6.134

4 Conclusion

Polyaniline-maghnite nanocomposites containing different polyaniline contents were prepared by intercalation and oxidative polymerization of aniline into interlayer spacing of maghnite (Mag-H+) layers. Fourier Transform Infra Red analyses and UV-vis spectroscopy confirmed the successful synthesis of polyaniline chains, particularly by the narrowing of the Si–O stretching vibration band confirmed the interaction between PANI and the clay.

Maghnite-H+, proton exchanged montmorillonite clay is an effective initiator for the polymerization of aniline. In the polymerization, the solid catalyst was thought to act as an acid to generate cation species. Actually, the efficiency of the polymerization reflected the Lewis acidity of maghnite-H+. Two main advantages were shown in the polymerization system using the solid acid maghnite-H+, that the catalyst could be removed from the mixture of the products by simple filtration and recycled without a loss of catalytic activity.

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