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Research Article

Green Synthesis of Cationic Polyacrylamide Composite Catalyzed by An Ecologically Catalyst Clay Called Maghnite-H+ (Algerian MMT) Under Microwave Irradiation

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Abstract

In this study, a novel green cationic hydrogel of cationic polyacrylamide composite have been prepared and investigated. The synthesis of green cationic polyacrylamide composite was evaluated for its solubility in water. The reactions were performed using acrylamide monomer, solvent, catalyst (clay fin called maghnite) and solution of H_2SO_4 (0.25 M), with the system under microwave irradiation (160 °C) for 4 min. Major factors affecting the polymerization reaction were studied with a view to discover appropriate conditions for preparation of the composite. The cationic polyacrylamide obtained is the subject of future studies of modification and transformation. The resulting polymer has been characterized by a variety of characterization techniques, such as: Fourier Transform Infrared Spectra and ^{1}H NMR spectra. Copyright © 2016 BCREC GROUP. All rights reserved

Keywords: cationic polyacrylamide; hydrogel; Maghnite-H+; green chemistry; microwave irradiation

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1. Introduction

Green Chemistry is the design of chemical products and processes that reduce or eliminate the generation of hazardous substances [1].The concept of greening chemistry is a relatively new idea which developed in the business and regulatory communities as a natural evolution of pollution prevention initiatives [2]. Cationic polyacrylamide is one kind of high efficiency emulsified flocculants with high concentration, cationic polyacrylamide main uses: (a) as paper retention [3]; (b) as water treatment chemical [4]. It is widely applied in improving the flocculation effect in the sludge dewatering processes like belt filtration and centrifugal separation [5]. It can improve the sludge treatment results, increase the degree of mud's dryness, and ensure the whiteness of water. Preparation of green cationic polyacrylamide under microwave irradiation is an important synthetic reaction for which a wide variety of procedure has been developed during the last years [6]. Cationic polyacrylamide is the linear polymer compound, because it has many active groups, but with many substances affinity, adsorption of hydrogen bond formation [7]. Inter-

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calation of polyacrylamide into interlayer spaces of natural montmorillonite called Maghnite (Algerian MMT) by the heterogeneous polymerization technique under microwave irradiation was studied. The modification was carried out with using both the raw and treated clay. It was shown that no initial modification of the layered mineral (by ion-exchange with Na+ cations or organophilization) is needed for the successful introduction of hydrogels into the interlayer gallery. The polyacrylamide materials exhibited a tendency to the formation of exfoliated structure [8].

Microwave irradiation has been widely used in the synthesis of organic-inorganic hybrid materials because of its well known advantages over conventional synthetic routes. Microwave heating has been proven to be of benefit particularly for the reactions under "dry" media (i.e. in the absence of a solvent, on solid support with or without catalysts) and offers a number of advantages: solvents are often expensive, toxic, difficult to remove in the case of aprotic solvents with high boiling point.

Moreover, the absence of solvent reduce the risk of explosions when reaction takes place in a microwave oven. Reactions under "dry" conditions (i.e. in the absence of a solvent, on a solid support with or without catalysts) were originally developed in the late eighties [9]. Synthesis without solvents under microwave irradiation offers several advantages [10]. The absence of solvent reduces the risk of explosions when the reaction takes place in a closed vessel in an oven. Moreover, aprotic dipolar solvents with high boiling points are expensive and difficult to remove from the reaction mixtures [11]. During microwave induction of reactions under dry conditions, the reactants adsorbed on the surface of alumina, silica gel, clay [12]. Consequently, such supported reagents efficiently induce reactions under safe and simple conditions with domestic microwave ovens instead of specialised expensive commercial microwave systems [13]. The cationic polyacrylamide obtained is the subject of future studies of modification and transformation. The resulting polymer has been characterized by a variety of characterization techniques such as Fourier transform infrared spectra and ^{1}H NMR spectra.

2. Experimental Section

2.1. Materials

All reagents in this work were of analytical grade and used as received without further purification. H_2SO_4 (98%) was used as the initiator, which was obtained from Sigma Aldrich (French). The maghnite-Na+ (MMT) used in this work came from a quarry located in Maghnia (North West of Algeria) and was supplied by the company “ENOF” (Algerian manufacture specialized in the production of nonferric products and useful substances).

2.2. Catalyst structure

The x-ray powder diffraction profiles shown in Figure 1 exhibited the presence of other crystalline phases, such as: quartz, fieldspath and calcite in (raw-Maghnite). Under acid

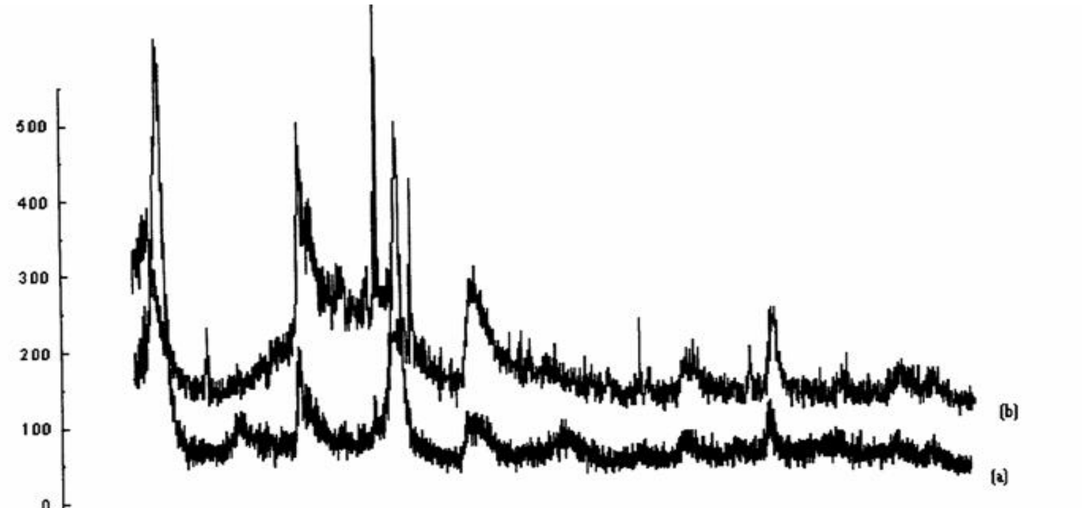


Figure 1. X-ray powder Diffraction of (a) Maghnite-Na+; (b) Maghnite- H+ 0.25 M

treatment, all trace of calcite was removed in “H-Maghnite”. The increase in basal spacing from 12.5 Å in “raw-Maghnite”, characteristic of a single water layer between the sheets, to a 15.02 Å value in “Maghnite” for two interlamellar water layers reflects the changes in interlayer cation and its associated hydration state as a result of the acid treatment [14].

The thermal characterizations of the composites include thermogravimetric analysis (TGA). Figure 2 shows the weight losses (%) versus temperature (°C) curves for pure Maghnite-Na+. The TGA of pure Maghnite-Na+ shows two stages of weight loss. The first weight loss in Na+-Mag below 100°C is a result of the release of free water. The second weight loss around 600 °C is associated with the dehydroxylation of silicate structure [15]. The total weight loss is only 13.94% up to 800 °C. As can be expected, Maghnite-Na+ shows a high thermal stability.

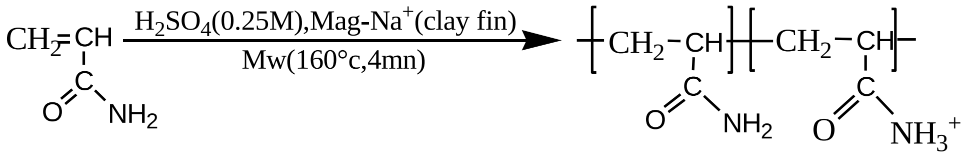
2.3. Synthesis of product

Maghnite-Na (2 %wt) was dissolved in aqueous solution of H_2SO_4 (0.25 M) and maintained under magnetic stirring. A (2 g) of acrylamide was then added. The reaction mixture was stirred vigorously for 5 min. The reaction mixture was then submitted to microwave irradiation at 160 ºC and for 4 min. After cooling, the reaction mixture was poured into distilled water and methanol. The oligomers were collected by filtration. The reaction taking place is shown in Scheme 1.

3. Results and Discussion

3.1. Characterization of products

The IR and ^{1}HNMR measurements were performed. The IR data of the samples is represented in (Figure 2). The IR spectrum of the product confirm the existence of the carbonyl, and amide functionalities indicated by the absorption peaks at 1657.6 and 3209.09-3344.13



Scheme 1. Synthesis of cationic Polyacrylamide (CPAM) induced by Maghnite-Na+ (2 %wt) under microwave irradiation.

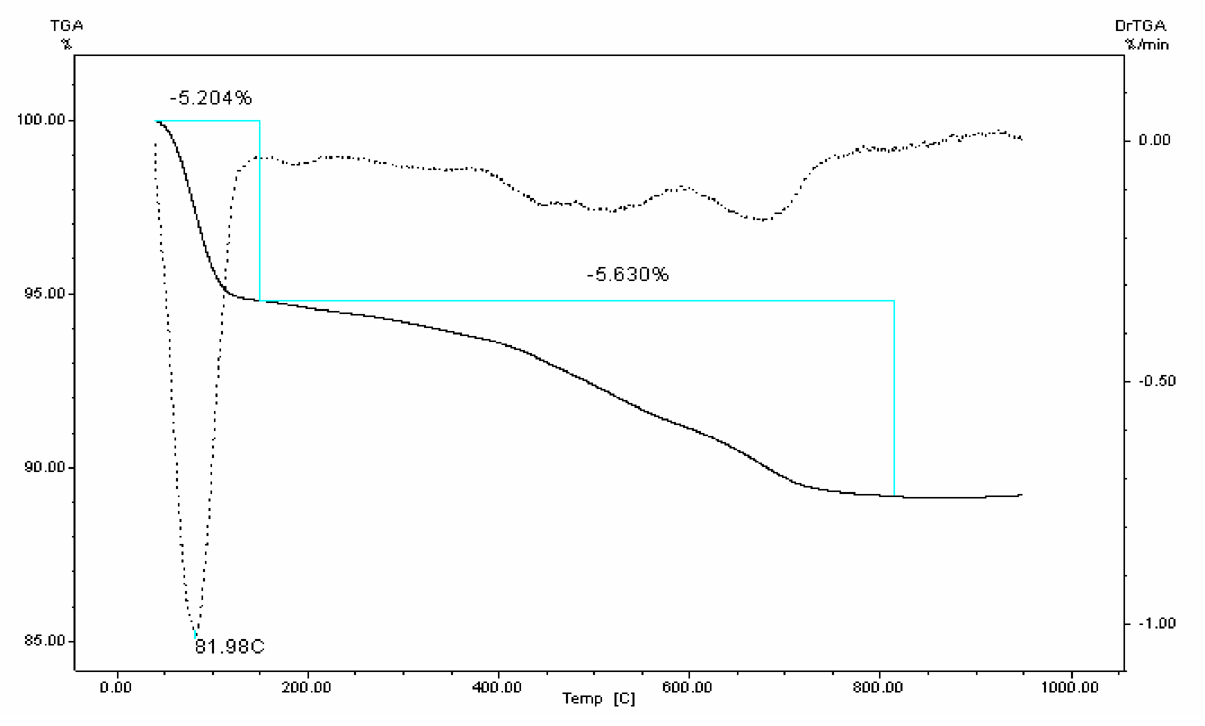


Figure 2. TGA curves of a Maghnite–Na+ obtained in nitrogen atmosphere at heating rate of 10 °C/min

cm^{-1}, respectively [16]. A typical presentation of ^{1}H NMR spectra of of the polymer is show in (Figures 3). The peaks at 1.2 - 1.4 ppm, 2.4 - 2.6 ppm, and 3.2 - 3.6 ppm denote the methyne, methylene, and amide proton in cationic polyacrylamide (CPAM) structure. The ^{1}HNMR and IR spectra (Figure 5) confirm the presence of reacted monomers in the interlamellar gallery of Maghnite (MMT).

3.2. Effect of the amount of Na+-Maghnite on the polymerization

Figure 6 Shows the effect of the amount of H+-MMT on the polymerization rate of (AM). Indeed, using various amounts of Na+-MMT, 0.5, 1.0, 1.5, 1.75 and 2 % by weight, the polymerization of (AM) was carried in free solvent under microwave irradiation (160 °C, 4 min). The amount of catalyst (H+-Mag) was an important

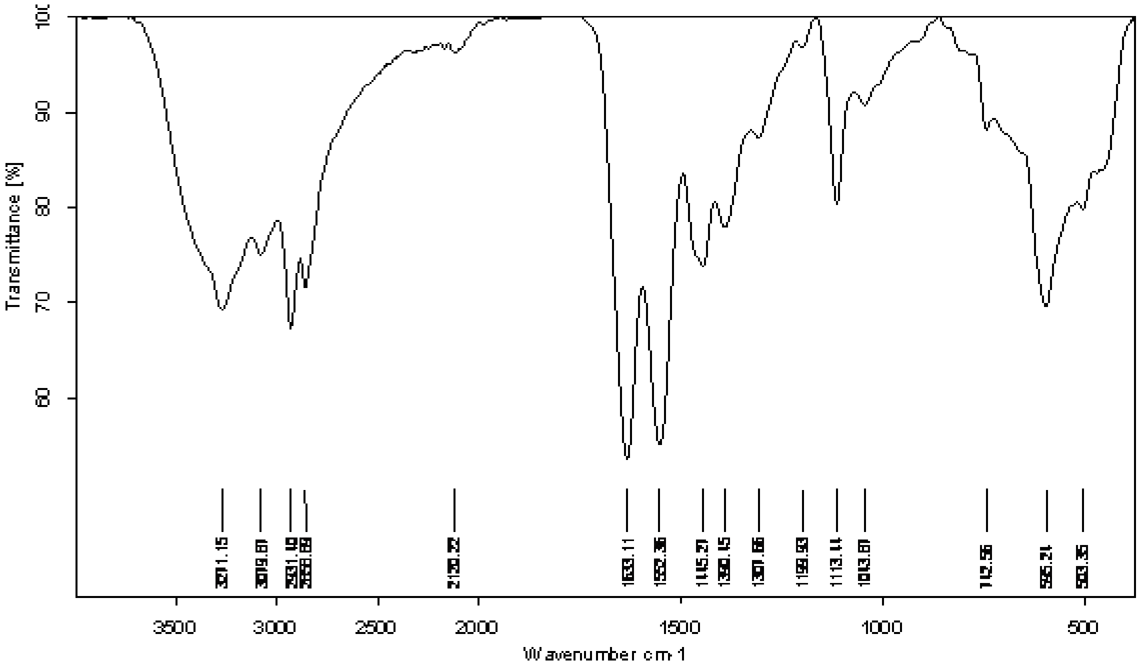


Figure 3. FTIR spectra of acrylamide (AM) monomer

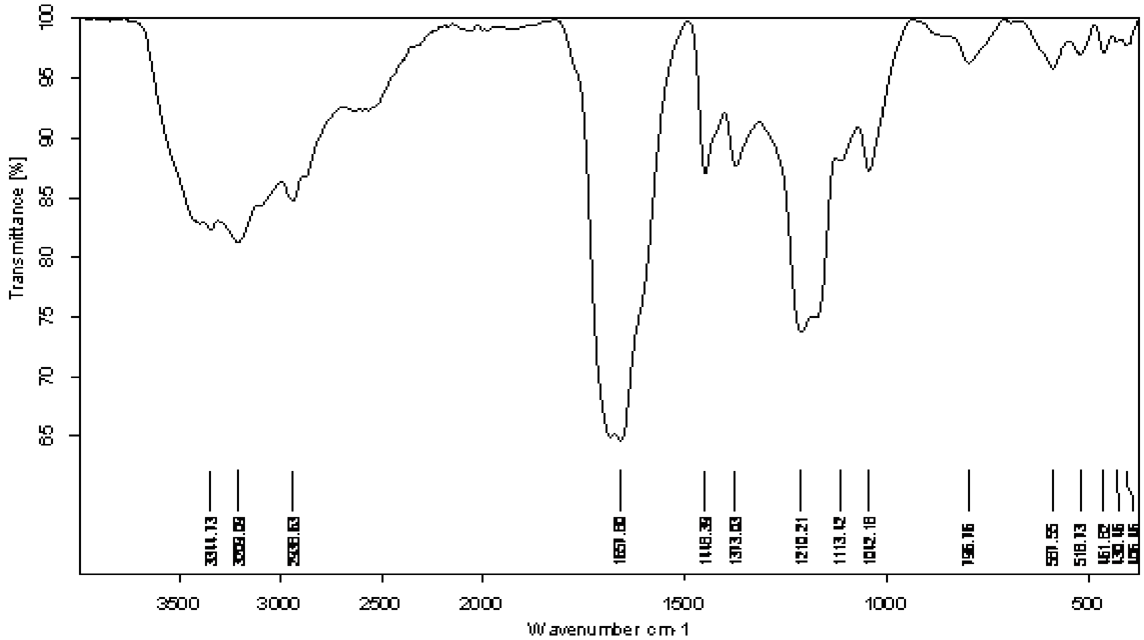


Figure 4. FTIR spectrum of cationic polyacrylamide (CPAM) induced by Maghnite-H+ under microwave irradiation

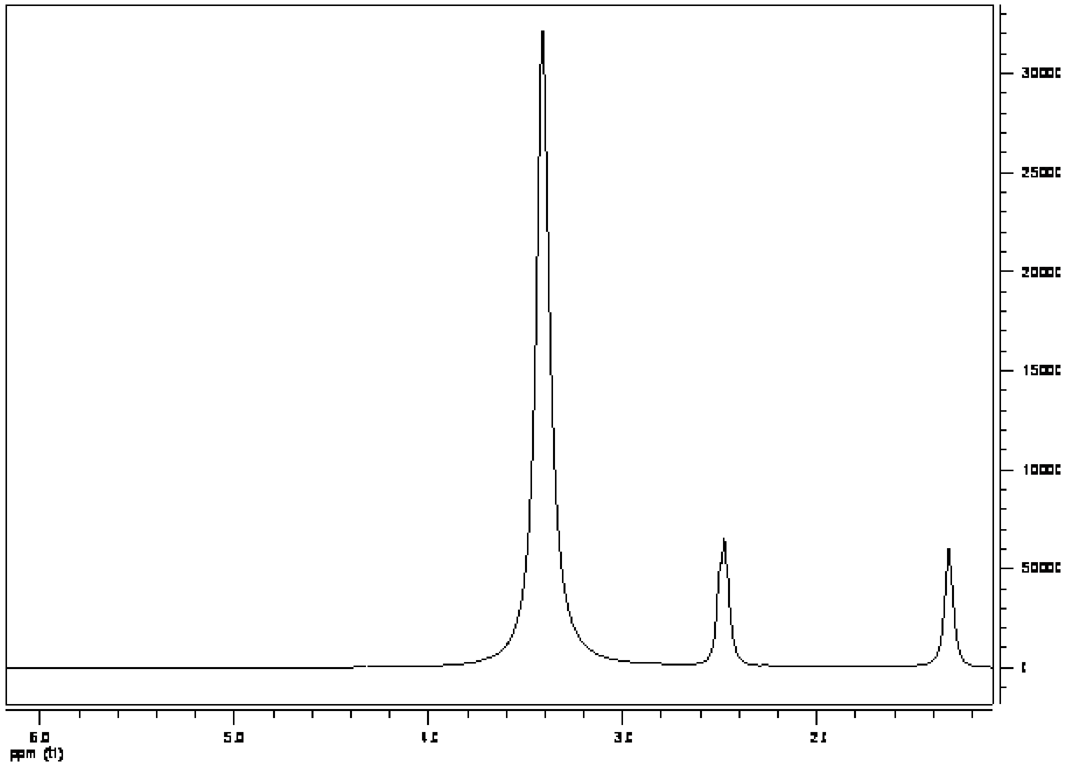


Figure 5. ^{1}H-NMR spectrum of cationic polyacrylamide (CPAM) induced by Maghnite-H+ in $CDCl_3$ under microwave irradiation

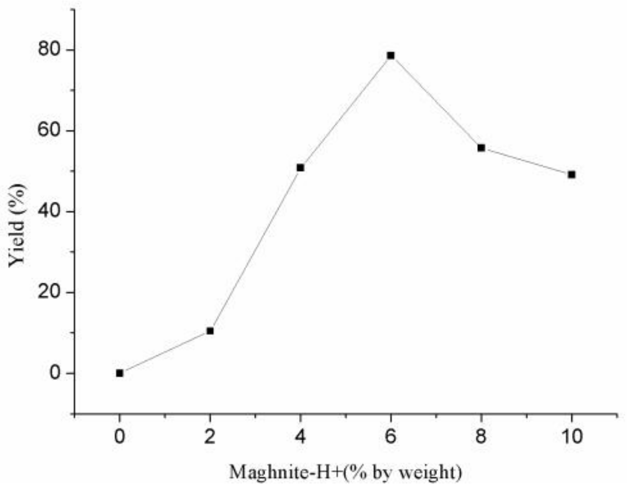


Figure 6. Effect of amount of catalyst on polymerization of cationic polyacrylamide

factor of polymerization. We can see from Figure 6, that the polymerization rate increased with the amount of Na+-MMT, in which the effect of Na+-MMT as a cationic catalyst for AM polymerization is clearly shown. This phenomenon is probably result of the number of "initiating active sites" responsible of inducing polymerization, and this number is prorating to the catalyst amount used in reaction. Similar results were obtained by Rahmouni *et al.* [17] and Ferrahi *et al.* [18].

4. Conclusions

Cationic polyacrylamide (CPAM) was synthesized via free solvent cationic polymerization under microwave irradiation and it's exfoliation ability has been evaluated in MMT-acid suspension. Here, a facile and effective strategy for the design and synthesis of green materials (polymer/clay) by an intercalation polymerization method in acid medium under microwave irradiation were developed. It was demonstrated that structure and thermal stability of cationic composite polyacrylamide depend on the ratio of monomer/clay and the temperature optimized. These strategy of free solvent and green chemistry will be a subject of our investigations in the future.

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References

[1] Ye, Q., Zhang, Z.C., Ge, X.W. (2003). Formation of monodisperse polyacrylamide particles by dispersion polymerization. I.Synthesis and polymer ization kinetics, *Journal of Macromolecular Science - Pure and Applied Chemistry* 39A(6): 545-556

[2] Cho, M.S., Yoon, K.J., Song, B.K. (2002). Dispersion polymerization of acrylamide in aqueous solution of ammonium sulfate: Synthesis and characterization. *Journal of Applied Polymer Science*, 83: 1397-1405.

[3] Chen, J., Park, H., Park, K. (1999). Synthesis of Superporous Hydrogels: Hydrogels with Fast Swelling and Superabsorbent Properties, *Journal of Biomedical Materials Research*, 44: 53-62.

[4] Liu, S.J., Lin, W.F., Chang, B.C., Wu, G.M., Hung, S.W. (1999). Optimizing the Joint Strength of Ultrasonically Welded Thermoplastics, *Advances in Polymer Technology*, 18: 125-135.

[5] Ye, Q., Zhang, Z.C., and Ge, X.W. (2003). Highly efficient flocculant synthesized through the dispersion copolymerization of water-soluble monomers induced by -ray irradiation: Synthesis and polymerization kinetics. *J. Appl. Polym. Sci.* 89(8): 2108-2115.

[6] Gemeinhart, R.A., Park, H., Park, K. (2000). Pore Structure of Superporous Hydrogels, *Polymers for Advanced Technologies*, 11: 617-625.

[7] Ye, Q., Zhang, Z., Ge, X. (2003). Highly efficient flocculant synthesized through the dispersion copolymerization of water-soluble monomers induced by γ-ray irradiation: Synthesis and polymerization kinetics. *Journal of Applied Polymer Science*, 89: 2108-2115.

[8] Colombani, D. (1997). Chain-growth control in free radical polymerization. *Progress in Polymer Science*, 22: 1649-1720.

[9] Shan, G.R., Cao, Z.H. (2009). A new polymerization method and kinetics for acrylamide: Aqueous two-phase polymerization. *Journal of Applied Polymer Science*, 111:1409-1416.

[10] Fang, D.B., Guo, R.W., Ha, R.H. (2006). Acrylamide polymer. Chemical Industry Press, Beijing.

[11] Rahmouni, A., Harrane, A., Belbachir, M. (2012). Thermally stable forms of pure polyaniline catalyzed by an acid-exchanged MMT clay called Maghnite-H+ as an effective catalyst. *International Journal of Polymer Science*. 846710 (doi:10.1155/2012/846710,2012)

[12] Liu, S.J., Chen, C.F. (2000). Optimization of Bubble Size in Rotationally Moulded Parts, *Plastics Rubber & Composites*, 29: 411-416.

[13] Gemeinhart, R.A., Park, H., Park, K. (2000). Pore Structure of Superporous Hydrogels, *Polymers for Advanced Technologies*, 11: 617-625.

[14] Belbachir, M., Bensaoula, A. (2006). US. Patent 7,094,823 B2 .

[15] Yahiaoui, A., Belbachir, M., Hachemaoui, A. (2003). Cationic Polymerization of 1,2-Epoxypropane by an Acid Exchanged Montmorillonite Clay in the Presence of Ethylene Glycol. *Int. J. Mol. Sci.* 4: 572-585.

[16] Hwang, S.J., Park, H., Park, K. (1998). Gastric Retentive Drug-delivery Systems, *Critical Reviews in Therapeutic Drug Carrier Systems*, 15: 243-284.

[17] Rahmouni, A, Harrane, A, Belbachir, M (2013). Maghnite-H+, an eco-catalyst layered (Algerian Montmorillonite) for synthesis of polyaniline/Maghnite clay nano-composites. *Int. J. Chem. Mater. Sci.* 1(6): 175-181.

[18] Ferrahi, M.I, Belbachir, M. (2003). Polycondensation of Tetrahydrofuran with Phthalic Anhydride Induced By a Proton Exchanged Montmorillonite Clay. *Int. J. Mol. Sci.* 4: 312-325.