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Performance Evaluation of Synthesized Crosslinked Poly (Acrylic Acid /Acrylate) Loaded with Magnesium Nanoparticles as a Conductive hydrogel

Enas M. Ahmed[1]*; Ahmed T. El-Aref[2] and Ahmed M. Awad[1]

[1] Department of Chemical Engineering & Pilot Plant,
[2]Department of Pre-treatment and Finishing,
National Research Centre, Cairo, Egypt

Abstract : Poly(Acrylic Acid /Acrylate) superabsorbent hydrogel (SAH) loaded with magnesium nanoparticles (Mg NPs) was synthesized via a free radical reaction using potassium persulphate (KPS) initiating system in presence of N,N`-methylenebisacrylamide (MBA) as a crosslinking agent and different concentrations of magnesium oxide. Swelling capacity of the prepared SAH was thoroughly investigated. Size and distribution of the nanoparticles and their dependence on the amount of magnesium oxide employed were also studied using Transmission Electron Microscopy (TEM). The morphology of the prepared dry SAH products was characterized by Scanning Electronic Microscopy (SEM) whereas the chemical components of SAH products were investigated using EDAX under SEM microscopy. The results revealed that size distribution of magnesium oxide nanoparticles depends on magnesium oxide concentration in the reaction medium. On the other hand the conductivity of the prepared SAH was found to be in relation to the initial concentration of magnesium oxide.
Keywords: superabsorbent hydrogel; magnesium oxide; nanoparticles; conductivity.

Introduction

Superabsorbent hydrogels (SAH) are still being a very important issue in both academic and industrial fields due to their applications in several technologies. Hydrogel nanocomposites are cross-linked hydrophilic polymers containing nanoparticles having capacity to absorb, swell and retain large amount of water in their crosslinked networks.

In particular, superabsorbent hydrogels are known to be a class of macromolecular gels, obtained by chemical stabilization of hydrophilic polymers in a tridimensional network, in which the dispersed phase is water, present in substantial quantity[1]. Some superabsorbent polymer gels, also known as hydrogels or water crystals, have attracted much attention from a large number of researchers and experts in various research and developmental areas due to current employment in several fields[2]. Hydrogels have number of applications in agriculture, medicine, contact lenses, indoor wastewater treatments, and tissue engineering[2-4]. These products are also utilized in sensing applications in which the swelling or de-swelling of the material is converted into a measurable signal[5]. The sensitivity of hydrogels to a large number of chemical and physical factors including heat, light, electrical voltage, ionic strength, pH, biological, and chemical agents make them suitable for wide range of applications[6].

The intrinsic characteristics of nanoparticle are mainly determined by size, shape, composition, crystallinity and morphology. Nanoscale particles provide a narrow size distribution, which is required to obtain a uniform material response[7, 8]. Inorganic materials such as metal, metal oxides and metal hydroxides have attracted more insight over the last decade because of their ability to withstand severe process conditions[9, 10]. Metal oxides such as oxides of titanium, zinc, magnesium and calcium are of particular interest as they are not only stable under intensive process conditions but also regarded as safe materials to both human beings and animals as well[11].

Recently, attention is paid to the superabsorbent polymers to develop new ways of application such as conducting materials, sensors, biomaterials, wave-absorbing materials and releasing matters[12]**.** However, the interest on conducting polymers (or hydrogels) based on the superabsorbent hydrogel is rather few. A conducting hydrogel could be employed in fuel cells, supercapacitor, solar cell and re-chargeable lithium batteries[13-16] due to a number of reasons including better conductivity character, colloidal stability, low cost and simple preparation.

The present work was undertaken to develop a simple method for the synthesis of magnesium nanoparticles embedded in SAH to produce SAH/Mg. The resulting SAH products are characterized by TEM, SEM and EDAX analyses. Moreover, conductivity of SAH loaded with Mg are also evaluated and discussed in some details.

Materials and Methods

Materials

Acrylic acid (AAc) in the monomeric form produced by Sisco Research Lab. Pvt. Ltd., India, potassium hydroxide (KOH) supplied by Sigma–Aldrich, Inc., N,N-methylenebisacrylamide (MBAAm) as a crosslinking agent and potassium persulphate (KPS) as initiator. These reagents were used as laboratory grade chemicals and were employed without further purification.

Preparation of poly(acrylic acid/acrylate) superabsorbent polymer/Mg nanoparticles

Preparation of poly(acrylic acid / acrylate) superabsorbent polymer / Mg nanoparticles was carried out according to a procedure described elsewhere[12]**.** For loading Mg nanoparticles within the network, a known amount of MgO is dissolved in distillated water at 80 ^{o}C. The reaction mixture was prepared by mixing acrylic acid monomer with potassium hydroxide followed by addition of MBAAm as a crosslinker, and MgO solution. The mixture was stirred and heated up to 70 $^{\circ}$C in a water bath for 15 minutes, followed by addition of the initiator and kept under stirring for few minutes to complete the polymerization reaction.

Transmission Electron Microscopy (TEM)

Images of SAH/Mg hydrogel composites were recorded using a JEOL JEM-1230 electron microscope operating at an acceleration voltage of 100 kV. Specimens for TEM were prepared by the placement of a swollen sample of hydrogel on a 400-mesh copper grid followed by evaporation of excess water in air under ambient conditions (25 ± 1^{o}C).

X- Ray Diffraction (XRD)

X'Pert Pro. PANalyltical with monochromator kV = 45 kV, MA= 40m Holland Analysis of swelled SAH and SAH/Mg sample was conducted using to indicate the composition of each sample.

Scanning Electron Microscopy (SEM and EDAX)

The morphology of the prepared dry SAH/Mg was characterized by scanning electronic microscopy technique, Quanta fig. 250 micro analyzer. EDAX was used to analyze the chemical components in a SAH under SEM. This method detects the X-rays produced as a result of the electron beam interactions with the sample. Mapping of the distribution of the different chemical elements constituting the specimen can be obtained. X-ray data are processed to measure the percentage of each measured element present in the individual particles. Thus the compositional and morphological data are then combined data analyses.

Conductivity

Via the employment of a conductivity meter, Adwa Waterproof EC/TDC Testers AD31 & AD32, Romania. The conductivity of the prepared SAH and SAH/Mg are assessed.

Results and Discussion

The introduction of nanoparticles in the SAH network systems was considered as primary important approach in this respect due to its feasibility in various areas of application.

Transmission Electron Microscopy

The size and morphology of Mg nanoparticles embedded within the SAH matrix were determined through TEM imaging. Figures 1(a, b, c and d) show a TEM micrograph of SAH/Mg nanoparticles in different shapes and sizes formed during the preparation process. Size distribution of Mg embedded in SAH network was formed to be in range of 1 – 42 nm depending on MgO concentration. It is evident that numbers of Mg nanoparticles increased by increasing amount of MgO employed. Size distribution derived from TEM image in figure 1(a, b, c and d) revealed that the particle size for nanoparticles within SAH/Mg matrix lies between 1 and 8 nm, 3 and 22 nm, 3 and 24 nm and between 6 – 42 nm respectively depending on the initial concentration of MgO.

Figure 2 (a, b, c and d) shows a gradual increase in amount and size of nanoparticles which may be attributed to increase in initial amount of MgO. Increasing the amount leads to aggregate of nanoparticles and thus leading to increased size.

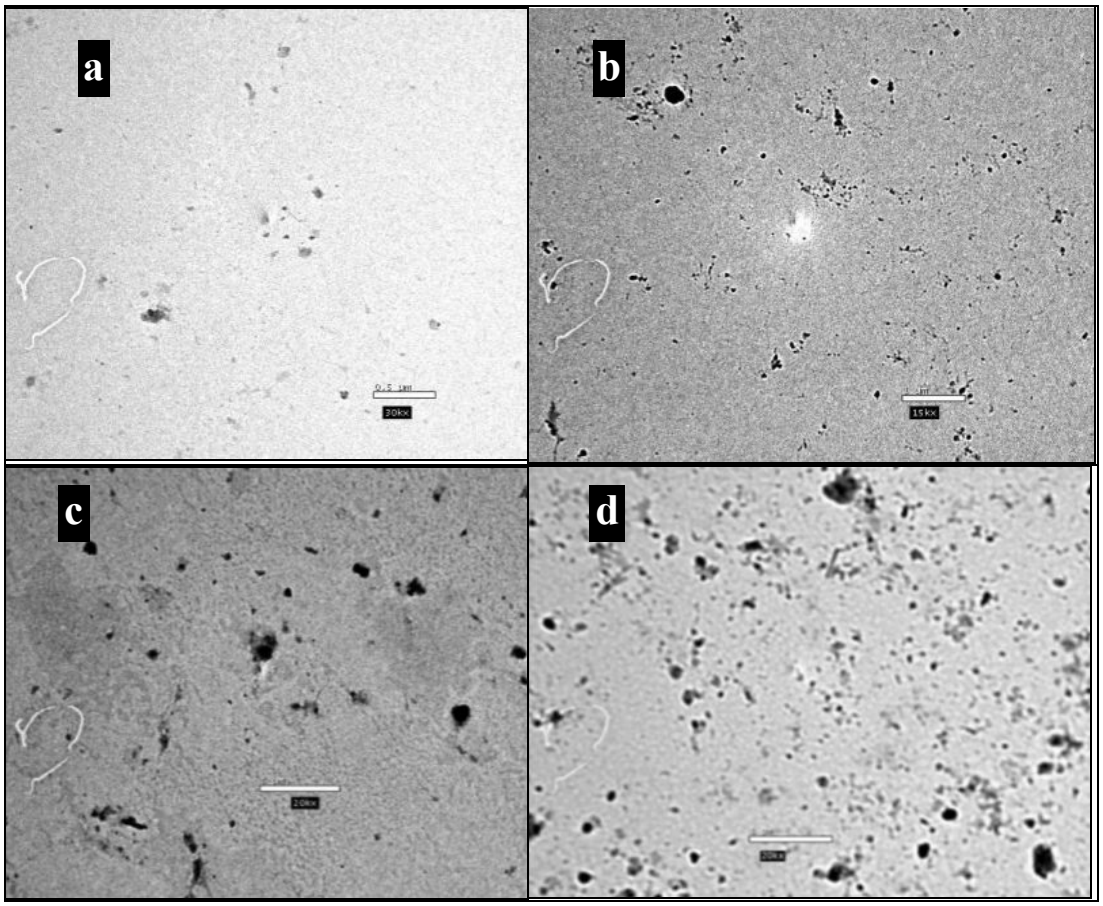


Figure 1: TEM images of the PAAc/AC hydrogel loaded with different amounts of magnesium oxide Nanoparticles (a) 0.1% MgO (b) 0.2% MgO (c) 0.3% MgO (d) 0.4% MgO.

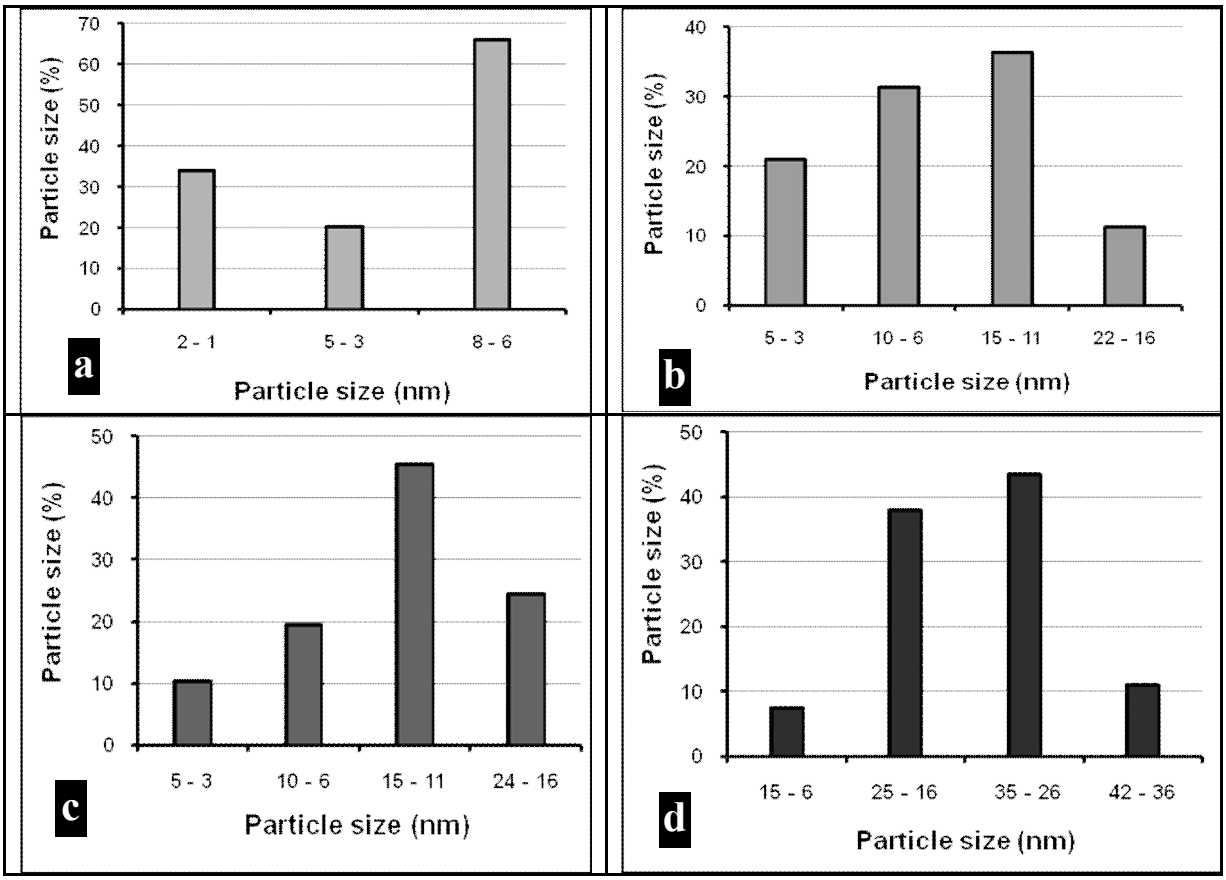


Figure 2: Histogram of MgO Nanoparticles distribution within SAH matrix related to MgO dose (a) 0.1%; (b) 0.2%; (c) 0.3% and (d) 0.4%.

X- Ray Diffraction (XRD)

The XRD pattern of SAH and SAH/Mg samples was used to determine the nanoparticle formation in SAH networks. Conventional x-ray diffraction patterns were recorded and used for peak identification and phase determination of Mg. Figure 3 depicts the results of X-ray diffraction (XRD) of and SAH/Mg samples, where the chart is totally amorphous. SAH sample did not exhibit a slight peak in XRD patterns, attributed to the polymer networks as shown in figure 3 (curve a) and no peaks were observed, this indicates the presence of hydrogel structure only. In contrast, Figure 3 (curve b) reveals the same behavior but, two small peaks at 2 θ = 29˚ and 41˚ of a cubic crystal structure were observed. This indicates the presence of magnesium atoms. The chart of XRD reveals the presence of magnesium atoms with weak crystallinity due to the penetration at room temperature. The magnesium ions were penetrated into SAH lattice and settled into it and may be covered or coated with SAH, so the peaks were appeared at $2\theta = 29^{\circ}$ and 41˚ and the expected sharp peak was ceased. This supports the prediction that magnesium atoms are penetrated and distribution into the SAH network. This leads to the conclusion that the presence of Mg into SAH takes place under the adsorption (reverse osmosis) force and embedded into the lattice as Mg atoms.

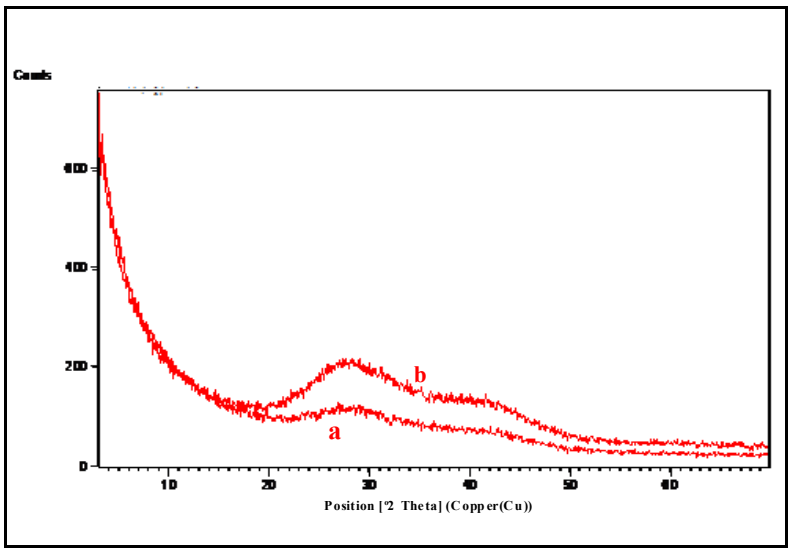
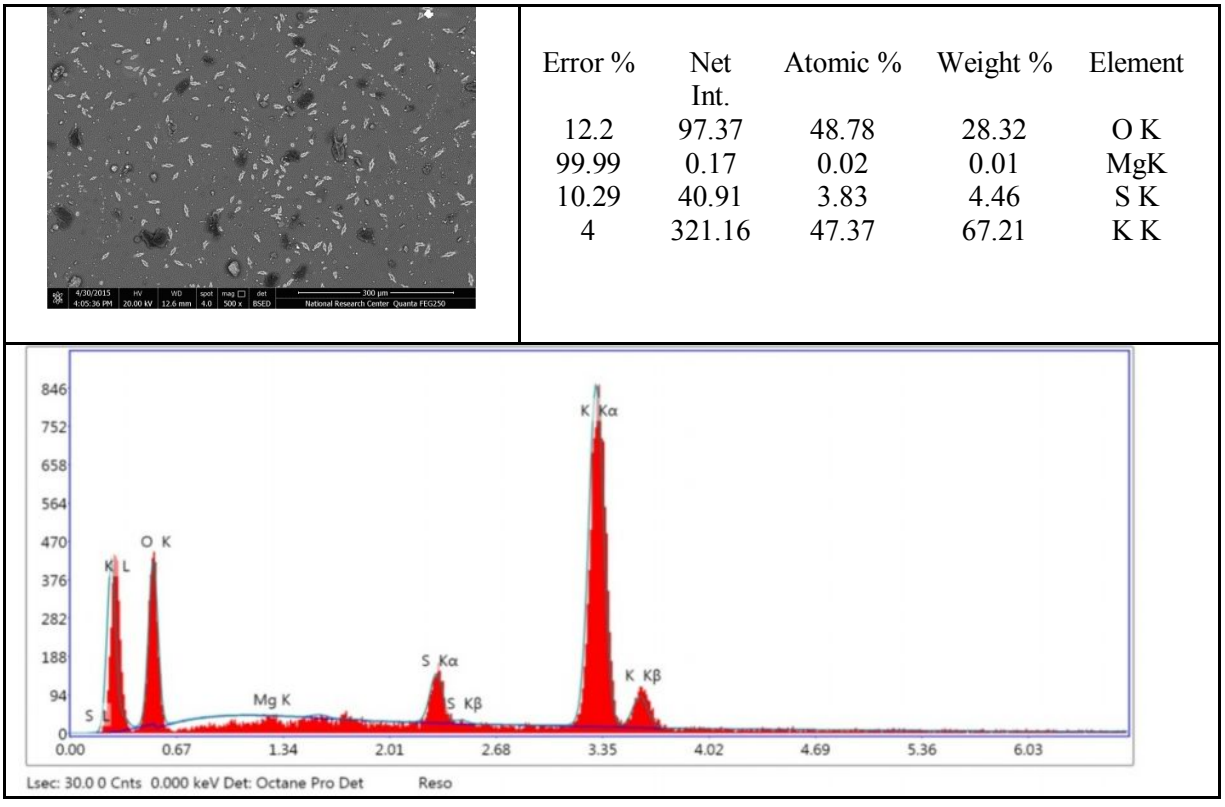


Figure 3: XRD of (a) SAH and (b) SAH/MgO

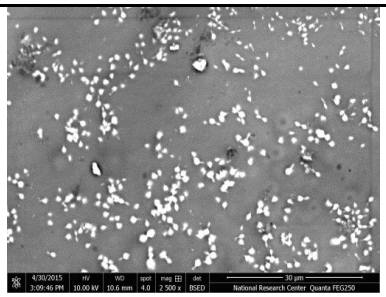
SEM and EDAX analyses

Scanning electron microscopy is at widely employed technique used for investigation of the shape, size and morphology of the hydrogel matrices. Figures 4, 5, 6 and 7 show SEM & EDAX analyses of the dried SAH loaded with different amounts of Mg nanoparticles the weight percentage of each element in the lattice of SAH molecules, where EDAX analysis detected 0.01 %, 0.08 %, 0.19 % and 6.47 % of Mg by weight depending on the initial concentration of MgO embedded in SAH during the preparation processes.



Error %	Net Int.	Atomic %	Weight %	Element
12.2	97.37	48.78	28.32	O K
99.99	0.17	0.02	0.01	MgK
10.29	40.91	3.83	4.46	S K
4	321.16	47.37	67.21	K K

Figure 4: SEM & EDAX analysis of SAH loaded with 0.1 % MgO Nanoparticles.



Error %	Net Int.	Atomic %	Weight %	Element
16.03	25.17	27.96	13.84	O K
91.1	0.6	0.11	0.08	MgK
12.44	25.89	4.41	4.37	S K
4.32	247.8	67.53	81.71	K K

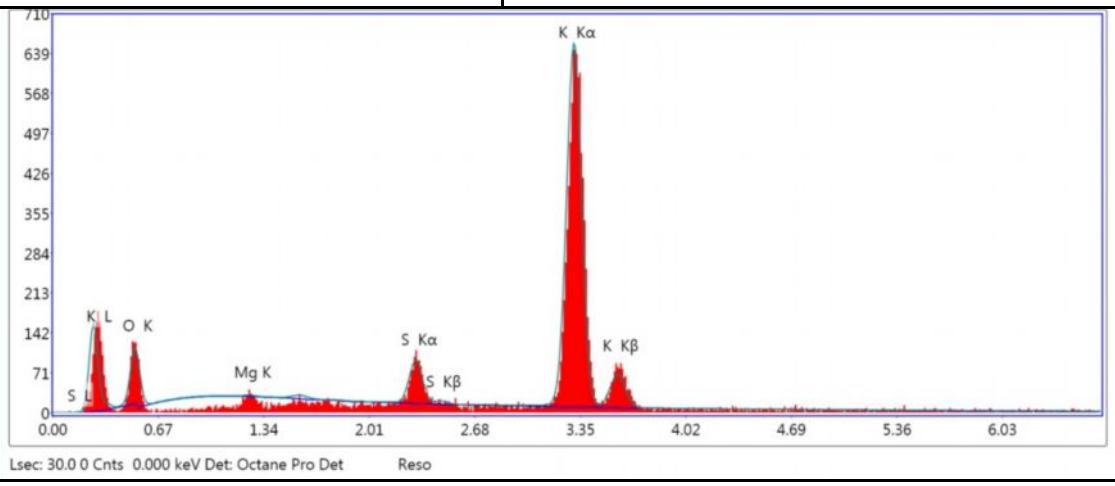
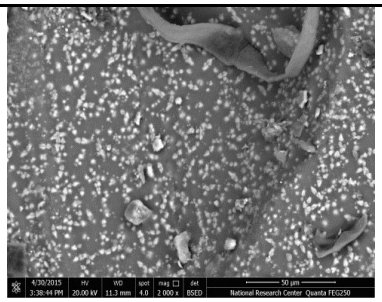


Figure 5: SEM & EDAX analysis of SAH loaded with 0.2 % MgO Nanoparticles.



Error %	Net Int.	Atomic %	Weight %	Element
8.92	57.78	28.77	13.79	C K
13.79	39.18	25.84	16.5	O K
73.92	1.7	0.19	0.19	MgK
10.55	32.39	3.64	4.66	S K
4.34	233.59	41.56	64.86	K K

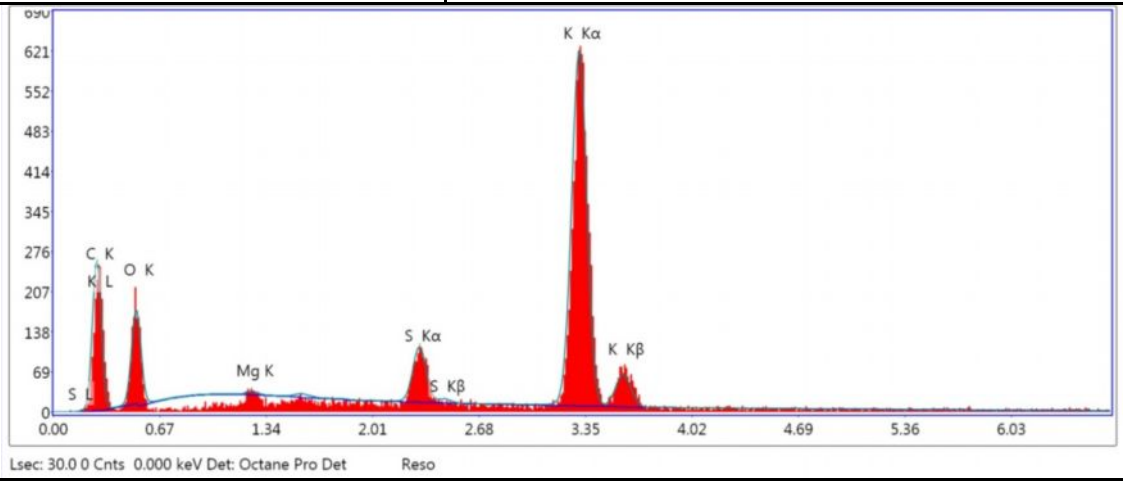
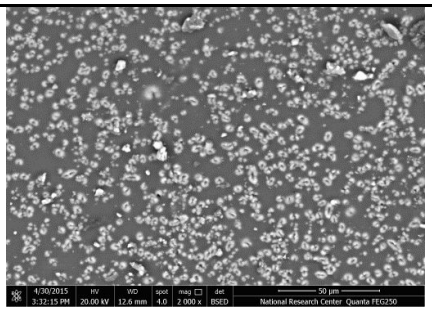


Figure 6: SEM & EDAX analysis of SAH loaded with 0.3 % MgO Nanoparticles.



Error %	Net Int.	Atomic %	Weight %	Element
10.46	191.18	62.37	41.92	O K
7.55	80.47	6.33	6.47	MgK
14.2	18.6	1.49	2	S K
5.39	128.96	14.54	23.89	K K
6.05	97.54	15.27	25.71	CK

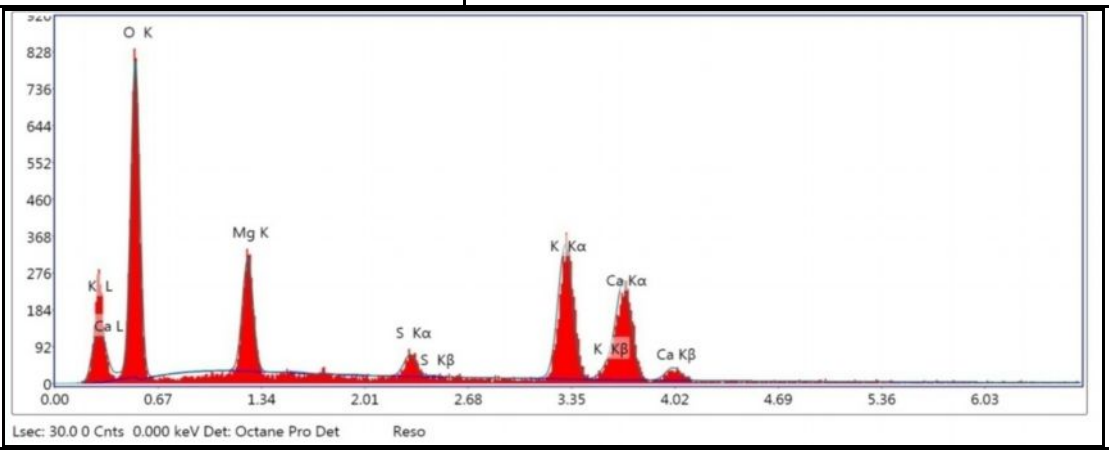


Figure 7: SEM & EDAX analysis of SAH loaded with 0.4 % MgO nanoparticles.

Conductivity

The interference of Mg particles and distribution all over the SAH structure leads to the increment of electric conductivity. The measurements of electric conductivity indicated that the conductivity of SAH was 2.57 ms, while as it was increased to higher values of 2.8 ms and 7.2 ms observed as the initial concentration of MgO increased from 0.1 to 0.4 %. This indicates that Mg particles were successfully trapped into the SAH matrix depending on the initial concentration. The distribution of Mg and hence the conductivity ensue from the presence of factors such as small atomic radius (0.160 nm)[17] of Mg and abundant H_2O molecules trapped into the hydrogel composition. So, it can be observed that the conductivity was improved as the initial MgO concentration increased as shown in Figure 8 and this is proved through the recorded results of TEM, XRD and EDAX.

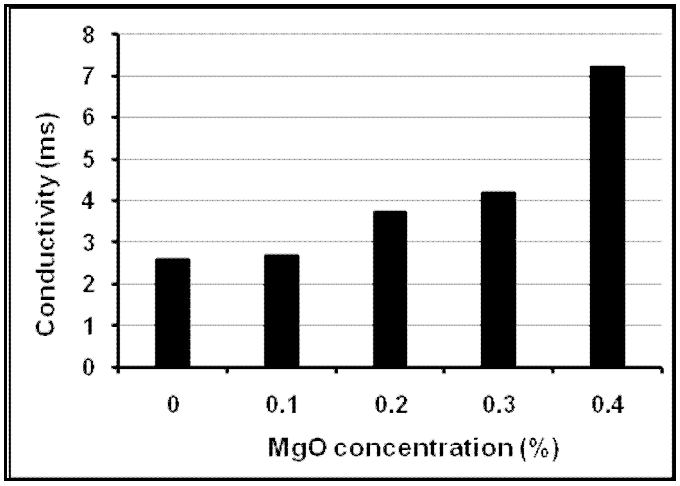


Figure 8: Conductivity of PAAc/Acrylate loaded with variable amounts of MgO.

The effect of swelling pH on SAH conductivity is illustrated in Figure 9**.** In general, the conductivity increases as initial MgO concentration increases. A maximum conductivity is attained at pH 8. Further increase in swelling pH leads to leveling off of conductivity values. This could be attributed to the high water content in the swollen SAH which reflects the ease of ions to diffuse inside the gel. The higher the water content, the higher the ionic diffusion rate[18]**.** The response of the SAH is also ascribed to the Mg present in the hydrogel, which results in an increase of the ionic distribution inside the network.

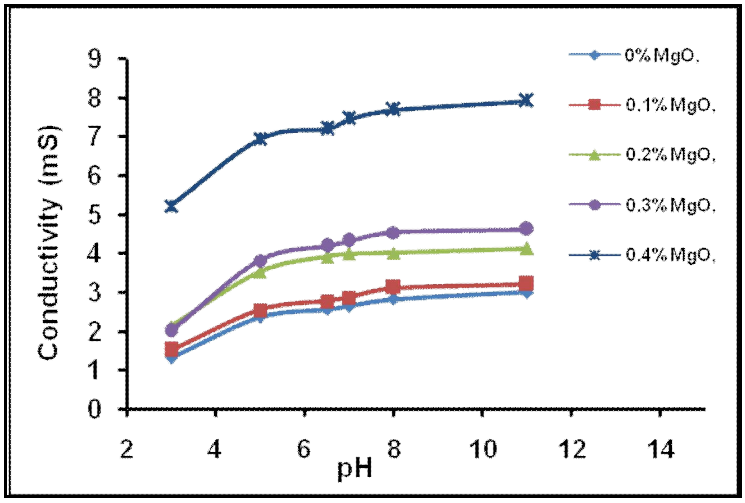


Figure 9: Effect of swelling pH on SAH conductivity

Conclusions

Poly(Acrylic Acid /Acrylate) superabsorbent hydrogel (SAH) loaded with magnesium oxide nanoparticles were successfully prepared via a free radical copolymerization, in presence of Magnisium oxide at varying concentrations along with concurrent, crosslinking to develop Mg nanoparticles in the hydrogel matrix. The hydrogel products were characterized for size distribution of Mg nanoparticles through examination of micrographs using Transmission Electron Microscopy. The results revealed that size and distribution of magnesium nanoparticles depend on initial concentration of magnesium oxide. The XRD pattern of SAH and SAH/Mg samples were used to determine the MgO nanoparticle formation in SAH networks. The morphology of the prepared dry SAH was also characterized by Scanning Electronic Microscopy (SEM) and EDAX and were utilized to analyze the chemical components in a SAH under SEM. EDAX analysis indicated that the presence of magnesium and related to the initial magnesium oxide concentration. The conductivity of the prepared SAH was found to be affected by presence of Mg nanoparticles in the matrix and the swelling pH.

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