



SYNTHESIS AND CHARACTERIZATION OF GUAR GUM GRAFTED POLY (ACRYLIC ACID)/ZEOLITE SUPERABSORBENT COMPOSITE BASED ON NATURAL POLYSACCHARIDE

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ABSTRACT

A novel biopolymer based superabsorbent composite was synthesized by carrying out graft copolymerization between guar gum and acrylic acid in the presence of zeolite using potassium persulphate as an initiator and N,N-methylene bis acrylamide as a cross linking agent. The small amount of inorganic fillers has been introduced to increase the absorption capacity of prepared composite. The composite was synthesized to be used as superabsorbent for the purpose of water absorption. Fourier transform infrared analysis confirms the reinforcement of polymer chains with zeolite sheets. The Thermal gravimetric analysis confirms the stability of composite. The composite was characterized by X-ray diffraction to study its crystalline nature. The Scanning electron microscopy analysis was used to study the morphology of composite. The water absorption capacity of superabsorbent was measured in distilled water by free swelling method as a function of percentage swelling and found to be 4880%. The effect of reaction parameters such as guar gum concentration, monomer concentration, initiator concentration, cross-linker concentration and pH on percentage swelling was also studied.

Keywords: Superabsorbent, Zeolite, composite, swelling, water absorption

INTRODUCTION

The Super absorbents polymers (SAPs) are cross linked hydrophilic polymers having a three-dimensional network structure which can absorb large amount of aqueous liquids (Buchholz and Peppas, 1994). It has been studied that the presence of hydrophilic groups, large free volume between polymeric chains and high polymer chain flexibility increases the swelling capacity of super absorbents polymers. Due to the distinctive properties they are extensively used in various fields such as horticulture and agriculture [Kosemund *et al.*, 2008 II] [Kasgöz and Durmus, 2008 III], bio-medical field and drug delivery system [Kiatkamjornwong *et al.*, 2002 IV]. The traditional superabsorbents are based on petroleum products which are not environmental friendly [Buchholz and Graham, 1997 V] Thus, new types of cost-efficient and eco friendly superabsorbent derived based on naturally raw materials have long been desired. The Graft copolymerization of monomers onto natural polymers is an efficient approach to achieve these materials. At present, natural macromolecules such as starch (Lanthong *et al.*, 2006 VI) cellulose, chitosan, gelatin, alginate, etc and their derivatives have been used as polymer matrix for preparing super absorbents.

Guar Gum (GG) is a hydrophilic, non-ionic polysaccharide extracted from the endospermic seed of the plant *Cyanopsis tetragonolobus*. It consists of a linear backbone of (1-4)-linked D-mannose units and is solubilised by the presence of randomly attached-(1-6) linked galactose units as side chains. GG and its derivatives form valuable ingredients for foods and pharmaceuticals (Wan *et al.*, 2007 VII). GG has better reactivity and can be easily modified by grafting acrylic acid monomers onto its backbone to derive new materials with improved structure and performance. The main functions of guar gum are as viscosifier, natural fibre, emulsifier, binding agent, stabilizer, thickener, gelling agent and flocculant (Sumit *et al.*, 2011 VIII).

Zeolites are hydrated aluminosilicate minerals that contain alkali and alkaline earth metals. The zeolites are noted for their lability toward ion exchange and reversible dehydration. They have a framework structure that surrounds interconnected cavities occupied by large metal cations and water molecules. The case of movement of ions and water within the framework allows reversible dehydration and cation exchange properties which vary with chemical and structural differences.

MATERIALS AND METHOD

Guar gum (GG, Shri Ram Gum Industries Basni, Jodhpur), Acrylic Acid (AA, Ases Chemicals, Jodhpur), N,N-Methylene bisacrylamide (MBA, Ases Chemicals, Jodhpur), Zeolite (Acetone (Fischer Scientific, Qualigens), Potassium persulphate (KPS, Sigma Aldrich) and Ethanol (C₂H₅OH, Emsure) All of these are used without further purification.

SYNTHESIS OF GUAR GUM-G-PAA SUPERABSORBENT COMPOSITE

In this paper, we have tried to synthesize and characterize the new superabsorbent composite guar gum-g-poly(acrylic acid)/zeolite and that was synthesized by using graft copolymerization in complete aqueous solution. The solution is stirred for about 15 mins to produce radicals. Further 1% (w/v) aqueous solution of N,N-methylene bisacrylamide (MBA) was added in the mixture. The reaction mixture was continuously stirred and heated at 60°C for about 3 hrs. After that it was precipitated using excess of acetone and kept overnight. It was washed several times with the mixture of distilled water and ethanol (60:40) to remove homo polymer and unreacted mass. The grafted polymer was dried in oven at 80°C. Finally, the dried resulting product was pulverized into powder by using pastel mortar.

ABSORBENCY OR SWELLING MEASUREMENT

Absorbency of superabsorbent composite is measured by the free swelling method and calculated in terms of percentage swelling. A 0.1 g of dry sample was immersed in distilled water at room temperature for 24 hr to reach swelling equilibrium. The swollen gel was taken out, dried between folds of filter paper (blotting) and weighed. After weighing the swollen samples, the equilibrium water absorbency of the superabsorbent was calculated using the following formula

$$\% \text{ Swelling} = (W_2 - W_1) / W_1 \times 100$$

W₁ and W₂ are the weight of dry sample and water swollen sample

RESULTS AND DISCUSSION

MECHANISM OF SYNTHESIS AND CHARACTERIZATION

The superabsorbent composite was synthesized by graft copolymerization of acrylic acid onto guar gum modified zeolite in presence of a cross-linking agent N,N-methylene bis acrylamide and potassium persulphate was used as an initiator. The persulphate is decomposed under heating and produced sulphate radicals that abstract hydrogen from –OH groups of the guar gum backbone. This peroxide-saccharide redox system thus results in active centers capable of initiating radical polymerization of acrylic acid (AA) to give a graft copolymer. Since a cross-linking agent, KPS is present in the system, the copolymer has a cross linked structure. The composite was characterized by FTIR to confirm grafting of AA onto guar gum modified zeolite.

FT-IR Analysis

The FTIR was carried out to study the functional groups and bonds characteristics of prepared superabsorbent polymer made by pelleting with KBr. The FTIR spectra of zeolite and grafted composite are shown in fig. 1 and 2. The mid-FTIR spectra of the synthesized zeolite in the region of lattice vibrations ($1,200\text{--}400\text{ cm}^{-1}$). A peak was observed at 1073 cm^{-1} attributed to stretching vibrations of Si-O groups. The bands at 778 cm^{-1} is of Si-O bending vibration in pure zeolite. Symmetric stretching of the external T-O linkages (T=Al or Si) occurred at 797 cm^{-1} , while the symmetric stretching due to the internal vibrations of the zeolite framework tetrahedra occurred at 695 cm^{-1} .

In the FT-IR spectra of composite, band position of stretching vibration of Si-O groups shifted from 1073 to 1057 cm^{-1} and the Si-O bending vibration shifted to 797 cm^{-1} . Additional IR bands observed at 3333.73 cm^{-1} and 1646 cm^{-1} are characteristics of O-H stretching and --C=O stretching vibrations respectively. The characteristics C-H stretching bands at 2925 cm^{-1} due to symmetric or asymmetric stretching vibration of --CH_2 groups of polymeric chain are also visible.

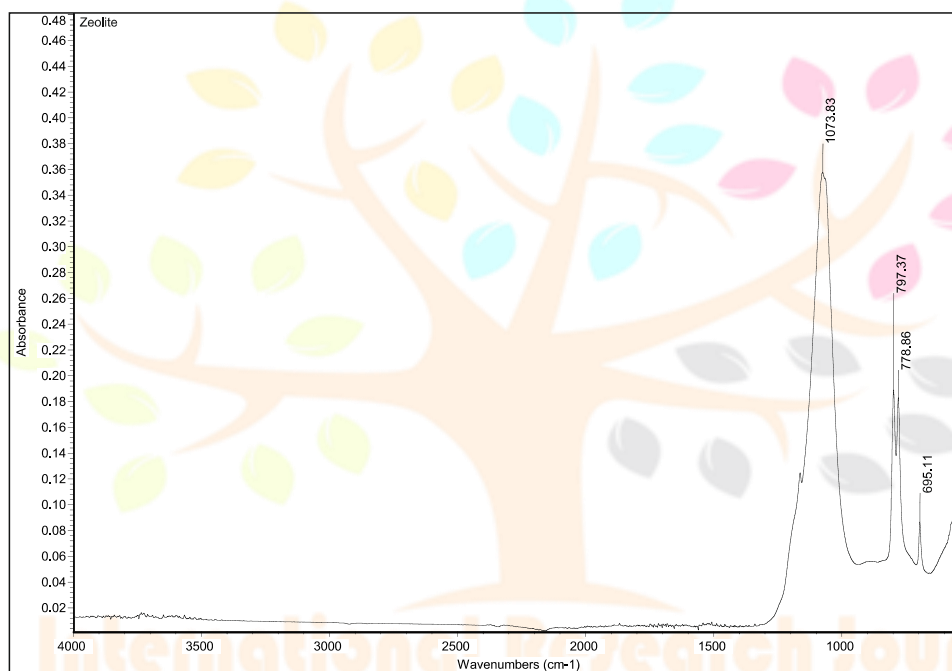


Fig. 1
FTIR of zeolite

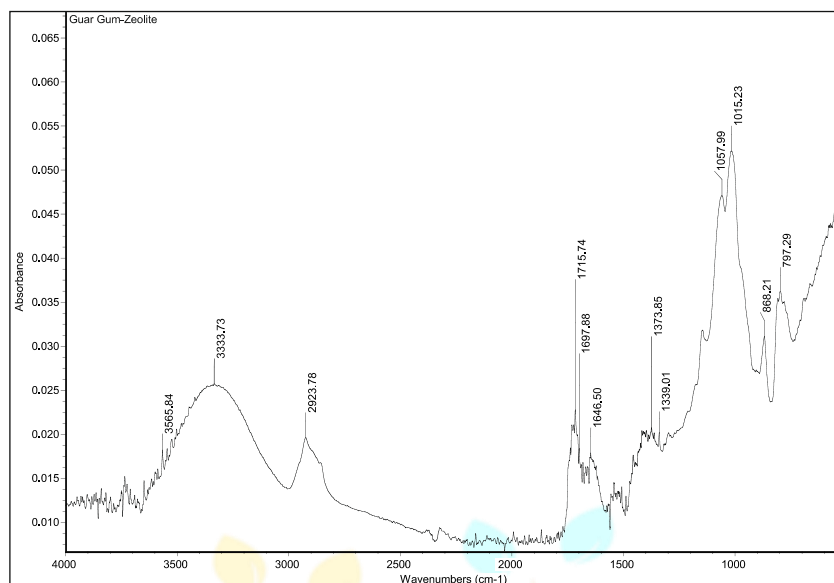


Fig. 2

FTIR of guar gum-g-poly (acrylic acid) /zeolite superabsorbent composite

XRD Analysis

X-ray diffraction (XRD) is a powerful technique for characterizing crystalline materials. The diffraction pattern was obtained with Philips X'pert pyrosystem *Copper K α* radiation at room temperature. The guar gum was largely amorphous and two peaks were observed at the scattering angle of 17.5 and 20.4. The grafted composite showed peak at scattering angle (2theta) of 20.32. The peak is sharp in nature. This shows the development of crystallinity in superabsorbent composite.

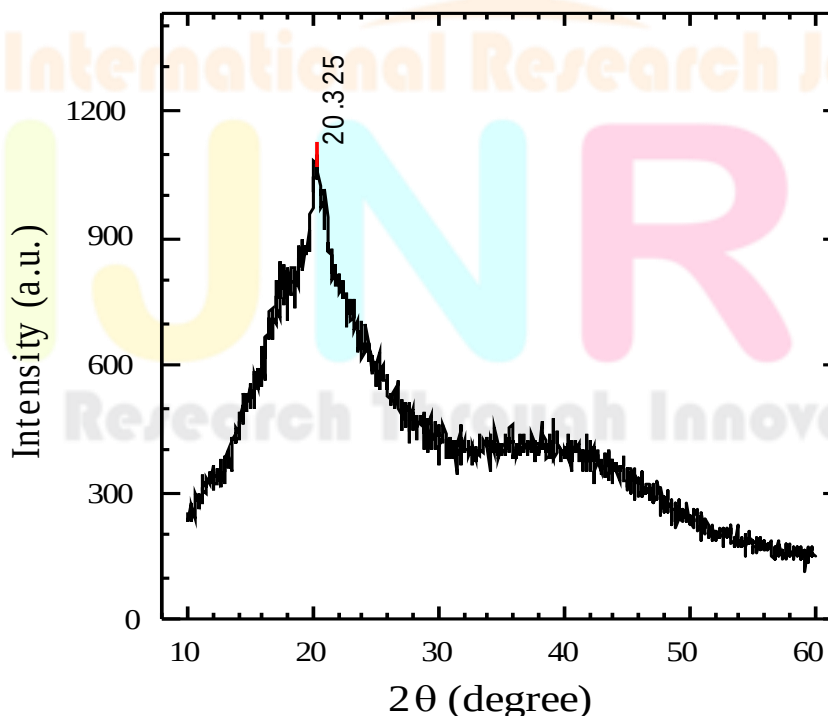
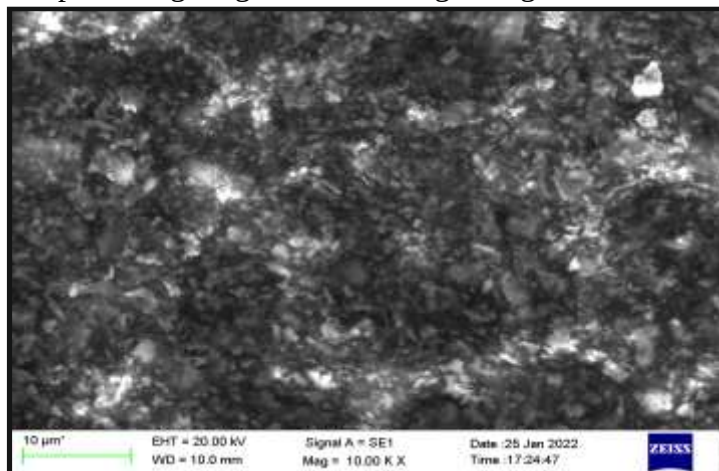


Fig. 3

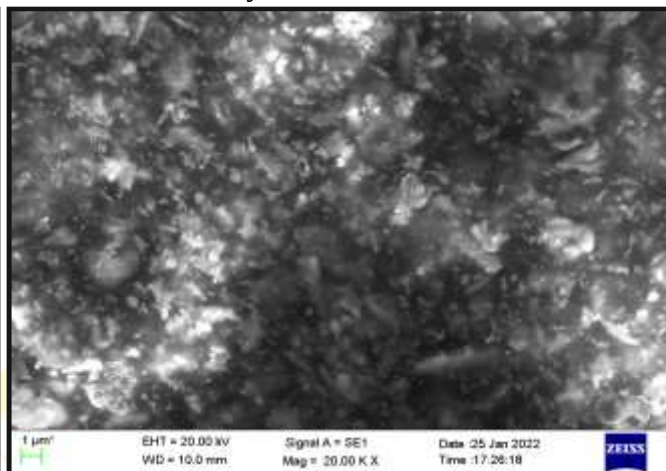
XRD of guar gum-g-poly (acrylic acid) /zeolite superabsorbent composite

SEM Analysis

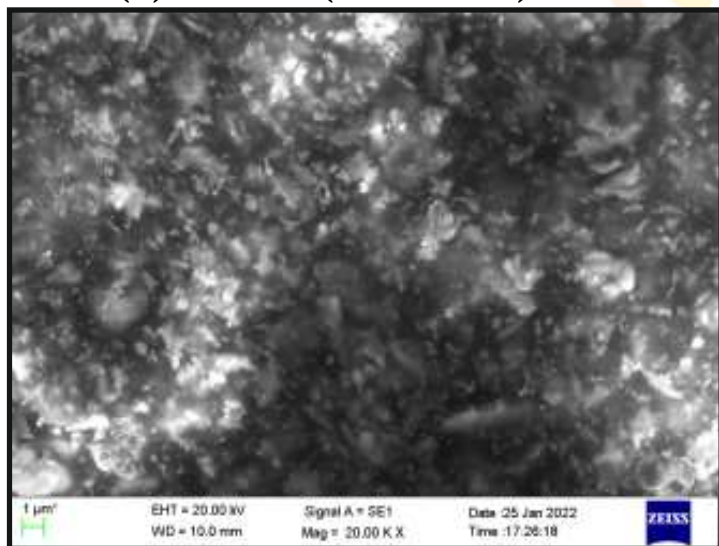
Scanning electron microscopy was used to analyzing surface morphology of composite. Fig.4 shows SEM composite at different magnification obtained by zeiss instrument. SEM observation reveals the prepared superabsorbent composite has uneven and coarse surface. It is clear that composite has more rougher structure as compared to guar gum and are in good agreement with our water absorbency observations.



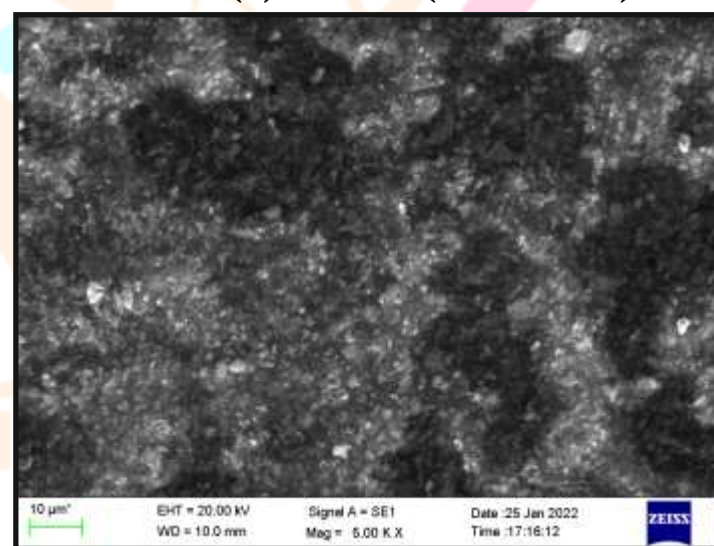
(A) ZEOLITE (MAG = 5K X)



(B) ZEOLITE (MAG= 10KX)

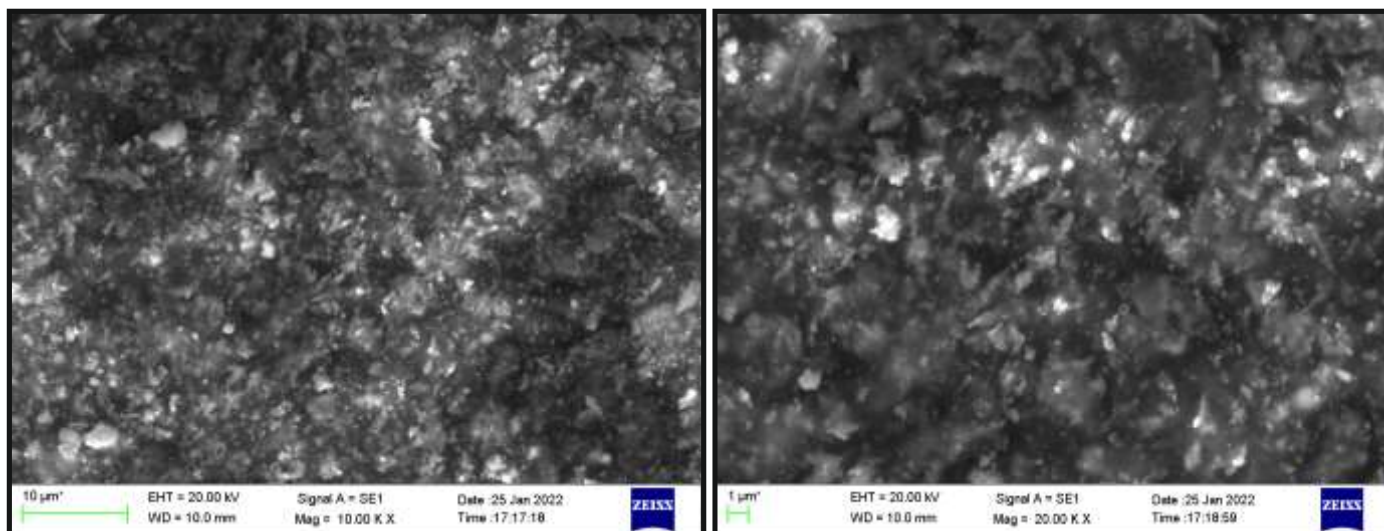


(C) ZEOLITE (MAG=20KX)



**(D) PAA/ GUAR GUM MODIFIED ZEOLITE
COMPOSITE (MAG = 5 KX)**

Research Through Innovation



**(E) PAA/ GUAR GUM MODIFIED
ZEOLITE COMPOSITE (MAG= 10 KX)**

**(F) PAA/ GUAR GUM MODIFIED ZEOLITE
COMPOSITE (MAG = 20KX)**

**FIGURE 4
SEM ANALYSIS**

TGA ANALYSIS

Thermo gravimetric analysis of composite was carried out using TGA Q 500 to study its thermal stability. Figure 5 shows the TGA curves of guar gum, GG-g-PAA composite. TGA of guar gum shows weight loss in two stages. The onset of thermal degradation occurs at 300°C with weight loss of 15% which is due to presence of moisture in sample. The second stage is degradation stage which occurs at 320°C with weight loss of 70%. In TGA curve of composite, thermal degradation occurs at 200°C with a weight loss of 15% which is the result of desorption of water. The composite shows 65% weight loss at 335°C.

There is about 75% weight loss at 550°C. TGA curve of PAA shows weight loss of 10% at 300°C. PAA shows 92% weight loss at 350°C. This shows the better thermal conductivity of super absorbent composite.



**FIGURE 5
TGA OF GG-g-POLY-AA/ZEOLITE**

INFLUENCE OF REACTION PARAMETERS

The Effect of Concentration of Guar gum, Acrylic Acid, MBA, KPS and pH on percentage swelling of superabsorbent was studied and results are shown in the following figures.

Influence of zeolite content on swelling behavior of composite

Figure 6 showing the effect of zeolite concentration on water absorbency of superabsorbent composite. When the zeolite concentration increases from 0.2% (w/v) to 1% (w/v). The increase in percentage swelling from introduction of zeolite can be because of the fact that zeolite particles acts as cross-linking agent. According to literature, ultrafine clay mineral powder act as additional cross-linking points in polymer networks. The zeolite prevents the tangle of graft polymeric chains and weakens the hydrogen bonding interaction among hydrophilic groups. The percentage swelling decreases after a particular concentration of zeolite (w/v) %.

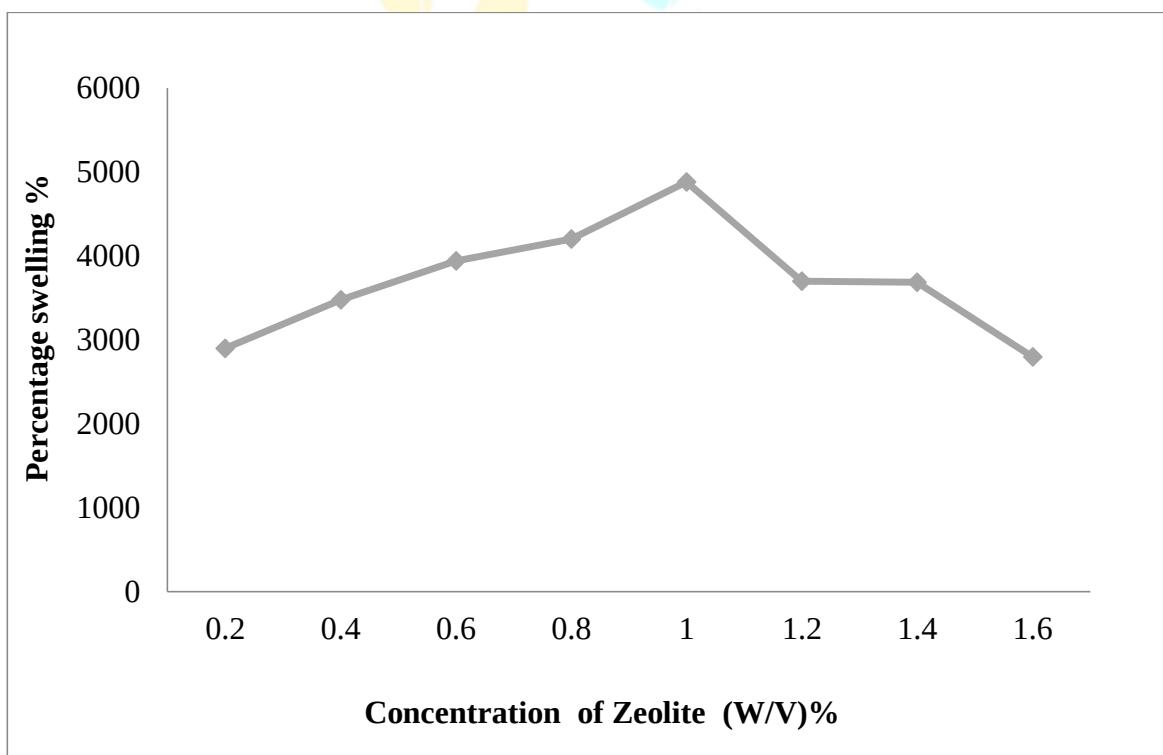


FIGURE 6

INFLUENCE OF CONCENTRATION OF ZEOLITE ON PERCENTAGE SWELLING OF GG-G-PAA/ ZEOLITE SUPERABSORBENT COMPOSITE (SAC)

Influence of saline concentration on swelling behavior of composite

The swelling behavior of composite was studied in different saline solutions. The percentage swelling of composite was studied in various solutions of NaCl and CaCl₂ solutions. The result indicates that water absorbency is found to be less as compared to distilled water. The water absorbency by composite was also found to be less in CaCl₂ solutions as compared to NaCl solutions. The reason for decrease in water absorbency is the fact that as the valency of cations increases neutralization of several charges inside the polymer by forming complex leads to increase in ionic cross-linking degree and results in loss of swelling of the composite.

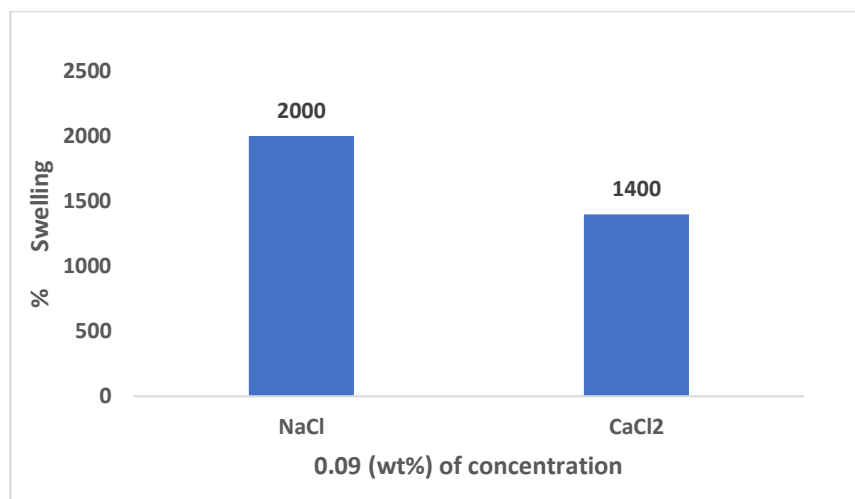


FIGURE 7

**INFLUENCE OF SALINE CONCENTRATION ON PERCENTAGE SWELLING OF GG-G-PAA/
ZEOLITE SUPERABSORBENT COMPOSITE (SAC)**

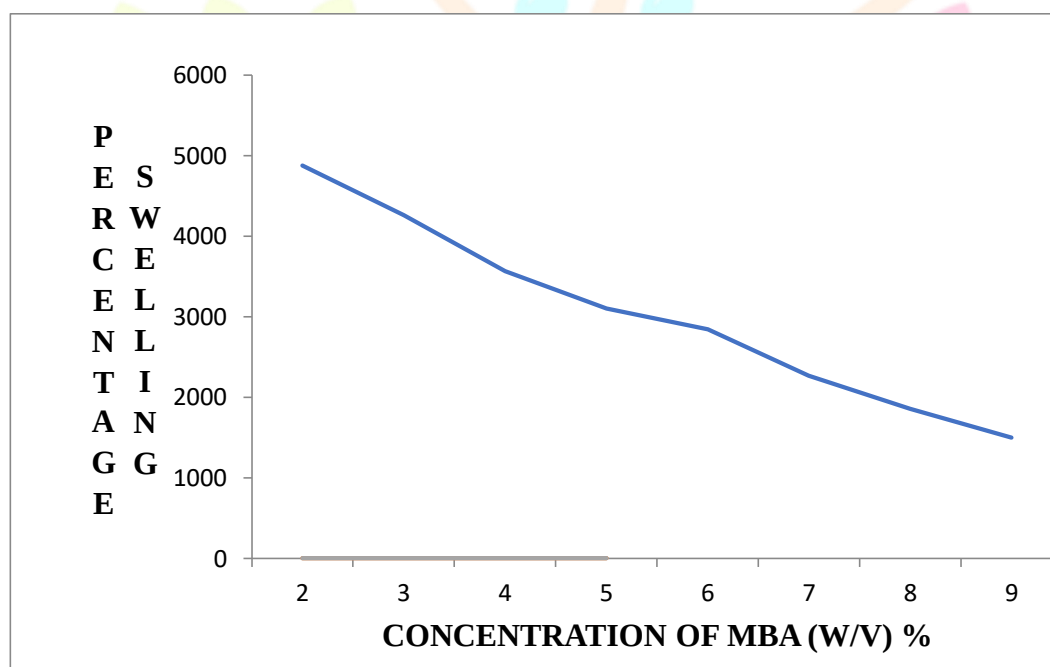
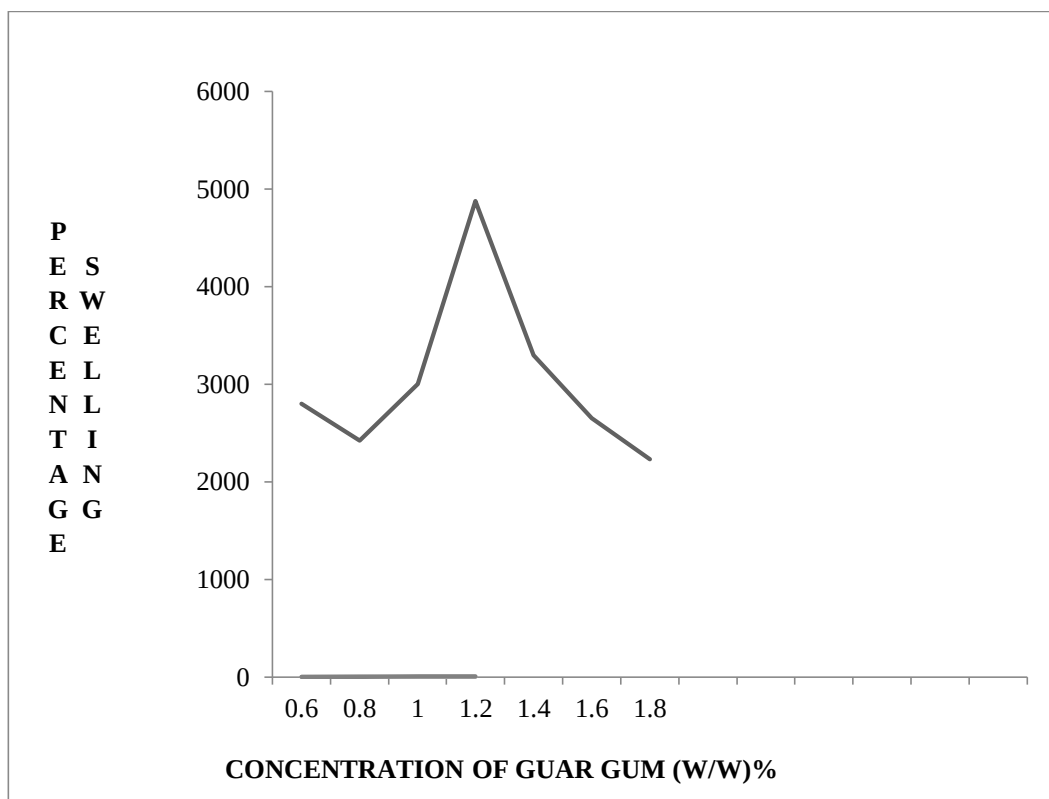
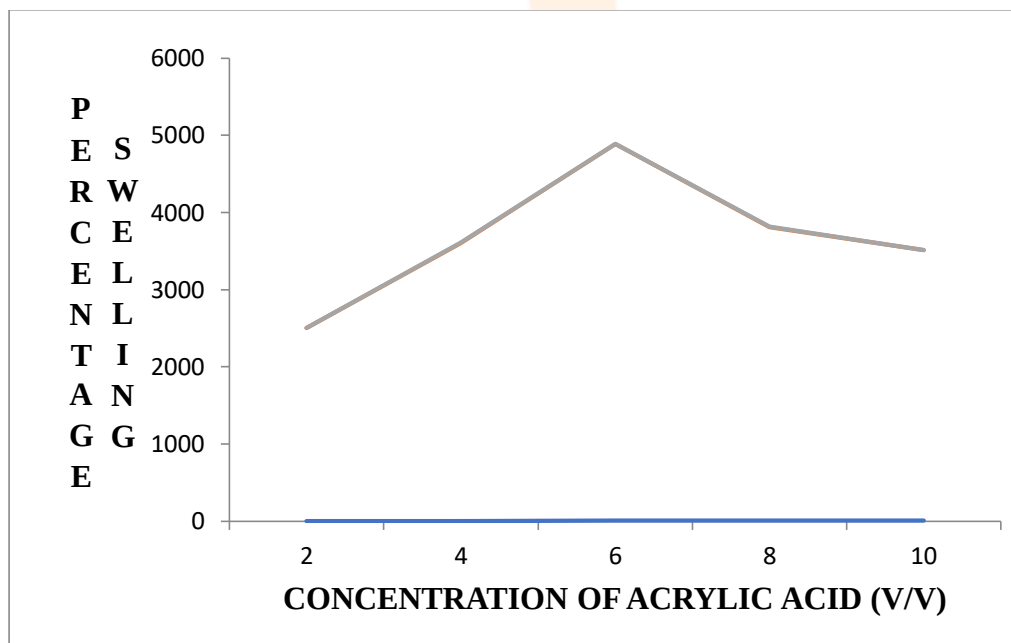


FIGURE 8

**INFLUENCE OF MBA CONCENTRATION ON PERCENTAGE SWELLING OF GG-G-PAA/ ZEOLITE
SUPERABSORBENT COMPOSITE (SAC)**

**FIGURE 9**

INFLUENCE OF GG CONCENTRATION ON PERCENTAGE SWELLING OF GG-G-PAA/ ZEOLITE SUPERABSORBENT COMPOSITE (SAC)

**FIGURE 10**

INFLUENCE OF ACRYLIC ACID CONCENTRATION ON PERCENTAGE SWELLING OF GG-G-PAA/ ZEOLITE SUPERABSORBENT COMPOSITE (SAC)

Conclusion

A novel superabsorbent composite prepared using guar gum modified zeolite and acrylic acid by graft copolymerization using MBA as a cross-linking agent, KPS as an initiator in complete aqueous solution to make it biodegradable and environmental friendly. The composite exhibits hydrophilic interactions. The composite was characterized by FTIR, TGA, XRD and SEM. The effect of concentration of guar gum, monomer, crosslinker, initiator and pH on water absorbency were investigated. It has been found that prepared superabsorbent composites have water absorbency of 4880% which has 1.2%(w/v) guar gum, 1% (w/v) crosslinker, 6%(v/v) monomer, 0.25% (w/v) of initiator at pH 8. The prepared superabsorbent composite can be used in various fields like agriculture, horticulture, removal of dyes, oil spill cleaning etc.

Conflict of interests

The authors declare that there is no conflict interest.

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