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Synthesis and characterization of superabsorbent composite based on natural polysaccharide

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ABSTRCTS

In this work, Superabsorbent composite was synthesized based on guar gum and acrylic acid by free radical graft copolymerization reaction using N,N-methylene bisacrylamide as a cross linking agent and potassium persulphate as an initiator in complete aqueous solution to make it environmental friendly. The composite was synthesized to be used as superabsorbent for the purpose of water absorption. Fourier transform infrared analysis was carried out to confirm grafting of acrylic acid onto guar gum. 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 4600%. 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: *Percentage swelling, Copolymerization, Grafting, Cross-linking.*

Introduction

The Super absorbents polymers (SAP_s) are cross linked hydrophilic polymers having a three-dimensional network structure and 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 (Ni *et al.*, 2009). Due to the distinctive properties they are extensively used in various fields such as horticulture and agriculture (Liang *et al.*, 2009; Kosemund *et al.*, 2008; Chauhan *et al.*, 2009; Kasgöz and Durmus, 2008; Tang *et al.*, 2009), bio-medical field (Sadeghi and Hosseinzadeh, 2008) and drug delivery system (Wang *et al.*, 2009; Kiatkamjornwong *et al.*, 2002). The traditional superabsorbents are based on petroleum products which are not environmental friendly (Buchholz and Graham, 1997). Thus, new types of cost-efficient and ecofriendly 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; Wu *et al*., 2000), cellulose (Suo *et al.*, 2007), chitosan (Zhang *et al.*, 2007; Mahdavinia *et al.*, 2004) gelatin (Pourjavadi *et al.*, 2007), alginate (Pourjavadi *et al.*, 2007) etc and their derivatives have been used as polymer matrix for preparing super absorbents. Guar Gum (GG) is a hydrophilic, nonionic polysaccharide extracted from the endospermic seed of the plant Cyanopsis

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tetragonalobus. 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, cosmetics and pharmaceuticals (Wan *et al.*, 2007). 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, thickner, gelling agent and flocculant (Sumit *et al.*, 2011). In this paper, we have tried to synthesize and characterize the new superabsorbent composite based on guar gum and acrylic acid in complete aqueous solution. The structure of guar gum is shown in Fig. 1.

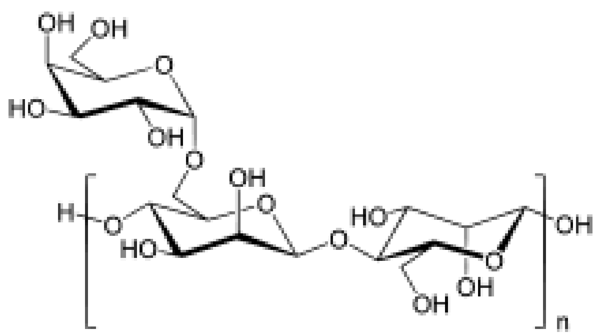

Fig. 1. Structure of Guar Gum

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), 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

Guar gum (GG) 1.8 % (w/v) was added in distilled water in a round-bottomed flask equipped with stirrer and thermostated water bath. The above solution was stirred for one hour. The monomer Acrylic Acid (AA) 6% v/v was added in above guar gum slurry and mixture was stirred for half an hour. The required volume of initiator potassium persulphate (KPS) 0.25% (w/v) was added and stirred at 40°C 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 Eq. (1)

$$\%Swelling = (W_2 - W_1) / W_1 \% \quad .. (1)$$

Swelling is the equilibrium water absorbency of sample which are the averages of three measurements. W_1 and W_2 are the weight of the dry sample and water swollen sample respectively

(a) (b)

Fig. 2. Showing dry composite (a) and swollen composite sample (b) respectively

Results and Discussion

Mechanism of synthesis and characterization

The superabsorbent composite was synthesized by graft copolymerization of acrylic acid onto guar gum in presence of a cross-linking agent N,N-Methylene bisacrylamide 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 AA to give a graft copolymer. Since a cross-linking agent, KPS is present in the system, the copolymer has a crosslinked structure. The composite was characterized by FTIR to confirm grafting of AA onto guar gum.

FT-IR Analysis

The assignments of the prominent peaks observed from the FT-IR Spectra of SAPs are shown in figure 4. Analysis of this data indicated the presence of monomer and crosslinker moieties in the the prepared SAP. In FTIR Spectra of native guar gum a broad band appears in the region of 3303.96 cm^{-1} shows the stretching vibration of O-H bond that shows the presence of large number of free hydroxyl groups in the guargum back bone. A sharp peak 1373.56 cm^{-1} and 1646.15 cm^{-1} shows bending vibration of $-CH_2$ and –OH groups respectively. The peak of 2887.78 cm^{-1} is due to $-CH_2$ stretching. The In FTIR spectra of guar gum grafted PAA composite, a broad peak appears at 3334.38 cm^{-1} which indicates stretching vibration of the –OH groups of guar gum. A peak appears 2923.05cm^{-1} is attributed to C-H stretching vibrations of PAA. In our spectra, a peak at 1011cm^{-1} is due to coupling of C-O stretching and O-H 'in plane' bending vibrations. There is distinct

Chain initiation and propagation Step

Chain Termination Step

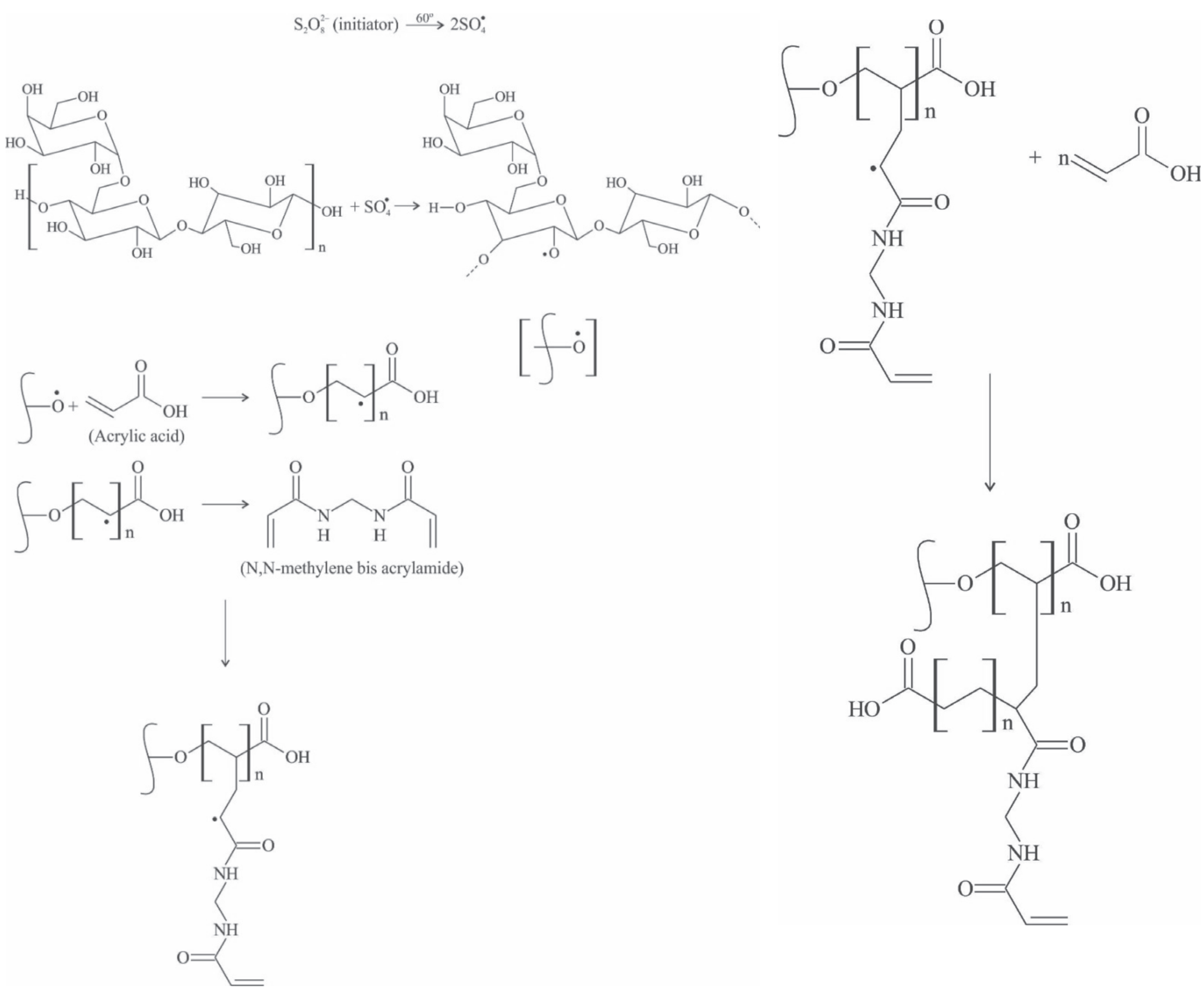

Fig. 3. General Mechanism of KPS initiated graft copolymerization onto guar gum in the presence of MBA.

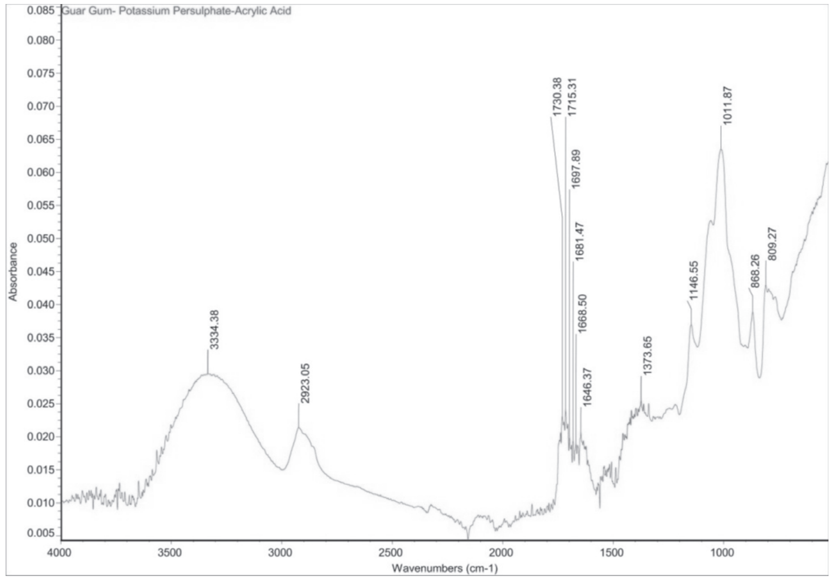

Fig. 4. FTIR of Superabsorbent composite

band from 1152 cm^{-1} to 1084 cm^{-1} which can be attributed to C-O-C stretching vibration of PAA. The presence of the characteristics peaks clearly proves that PAA has been successfully grafted onto the guar gum.

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*á* 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 two peaks at scattering angle (2theta) of 26.8 and 21.0. The peak is at 26.8 is sharp in nature. This shows the development of crystallinity in superabsorbent composite.

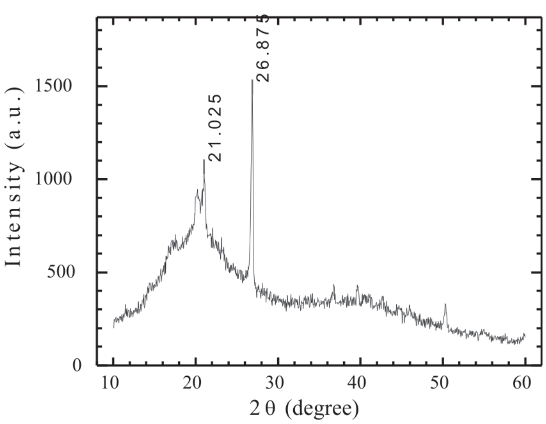

Fig. 5. XRD of Superabsorbent Composite

SEM Analysis

Scanning electron microscopy was used to analyzing surface morphology of composite. Fig. 6 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.

TGA Analysis

Thermogravimetric analysis of composite was carried out using TGA Q 500 to study its thermal stability. Fig. 7 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 300ºC with weight loss of 15% which is due to presence of moisture in sample. The second stage is degradation stage which occurs at 320ºC with weight loss of 70%. In TGA curve of composite, thermal degradation occurs at 200ºC with a weight loss of 15% which is the result of desorption of water. The composite shows 65% weight loss at 335ºC. There is about 75% weight loss at 550ºC. TGA curve of PAA shows weight loss of 10% at 300ºC. PAA shows 92% weight loss at 350ºC. This shows the bet-

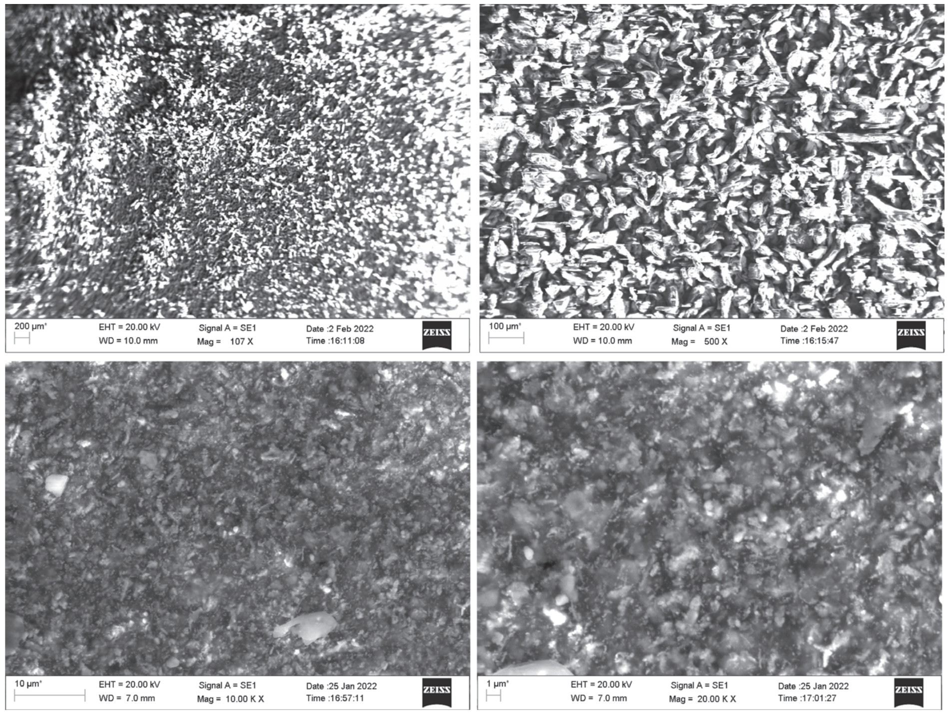

Fig. 6. SEM micrographs of (a) Guar gum (Mag = 107 X) (b) Guar gum (Mag = 500 X) (c) GG grafted PAA composite (Mag = 10KX) (d)GG grafted PAA composite (Mag = 20 KX)

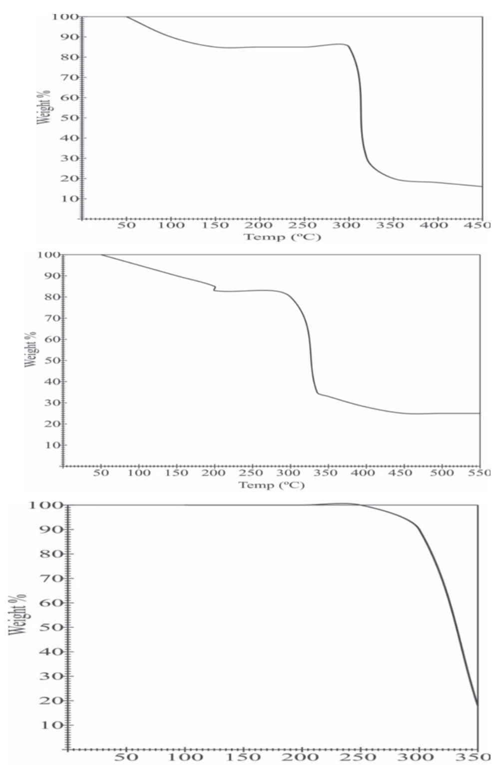

Fig. 7. TGA curves of (a) Guar gum (b) GG-g-PAA composite (c) PAA

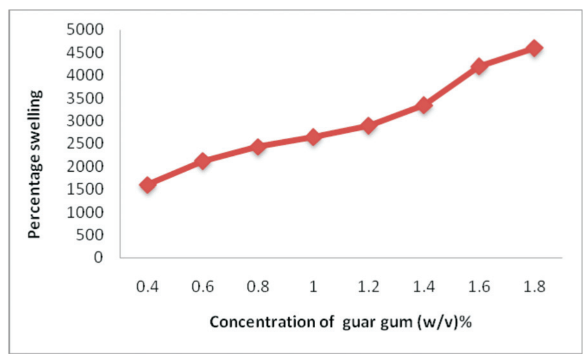

Fig. 8. Effect of guar gum concentration on percentage swelling of superabsorbent composite (SAC)

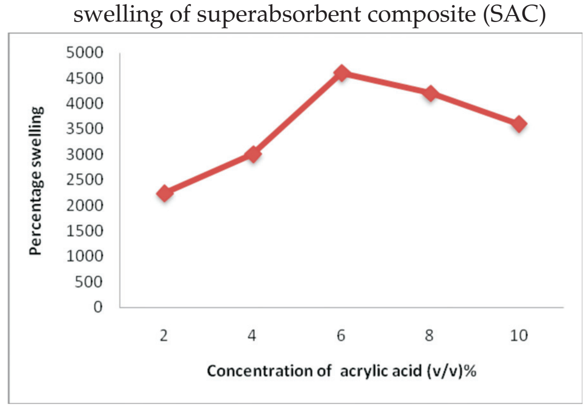

Fig. 9. Effect of concentration of Acrylic Acid on percentage swelling of superabsorbent composite.

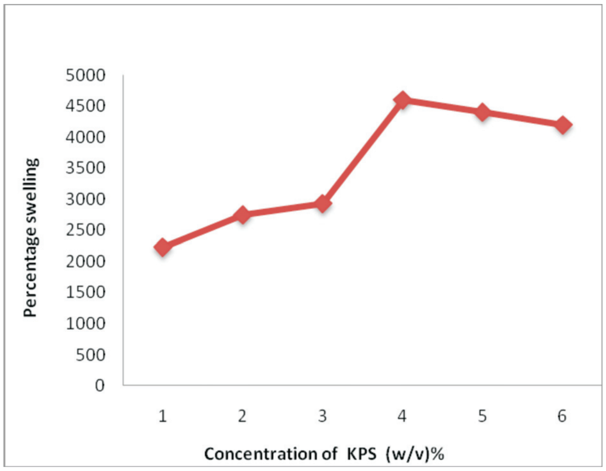

Fig. 10. Effect of concentration of KPS on percentage swelling of Superabsorbent Composite.

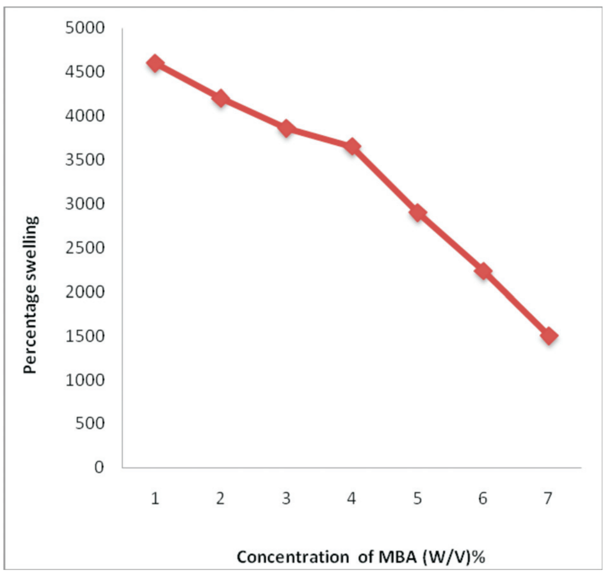

Fig. 11. Effect of concentration of MBA on percentage swelling of Superabsorbent Composite.

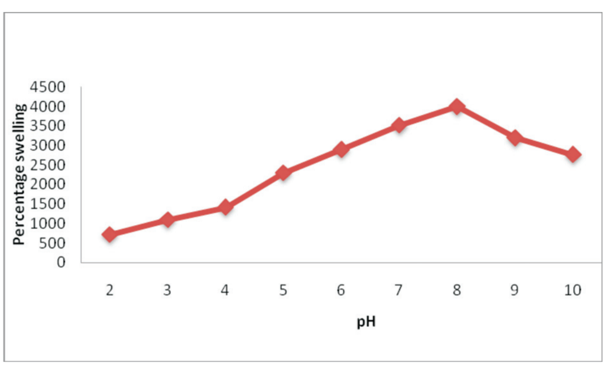

Fig. 12. Effect of pH on percentage swelling of Superabsorbent Composite.

ter thermal stability of grafted composite.

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.

Conclusion

A novel superabsorbent composite prepared using guar gum 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 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 4600% which has 1.8%(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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