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Preparation, Characterization and Swelling Properties of SuperabsorbentComposite Based on Guar Gum

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Abstract : In this work, cross-linked superabsorbent composite has been synthesized using guar gum and methyl methacrylate by graft copolymerization reaction in presence of potassium per sulphate (KPS) as an initiator and boric acid as cross linking agent in complete aqueous solution. FTIR analysis was carried out to confirm chemical structure of composite and SEM was used for morphological study. The composite was also characterized by XRD to study its crystalline nature. The water absorption capacity of superabsorbent was measured by free swelling method as a function of percentage swelling. The effect of reaction parameters such as guar gum concentration, monomer concentration, initiator concentration, cross-linker concentration and pH on swelling was investigated to achieve superabsorbent with improved water absorbency. Under the optimized conditions, maximum capacity of swelling in distilled water was found to be 3650%. The swelling behaviour of composite was also investigated in various saline solutions.
Keywords : Guar gum, percentage swelling, composite, potassium persulphate, superabsorbent.

1. Introduction

Superabsorbent can absorb and retain huge volumes of aqueous fluids even under some pressure compared with traditional absorbents (i.e. cotton, sponge, colloid silica) therefore it found extensive application in various fields including hygienic products, agriculture and horticulture, wastewater treatment and drug-delivery system etc.[1] Currently, most of the superabsorbent used in practice is mainly petroleum-based synthetic polymers with high production cost and poor environmentally friendly characteristics, and thus the study and development of natural polymer-based superabsorbents has become subject of great interest due to their commercial and environmental advantages.[2]Presently, many natural polysaccharides such as starch [3], cellulose [4], chitosan [5]and alginate [6] etc. and their derivatives have been used to prepare new type of superabsorbents.

Because of their exceptional properties i.e. biocompatibility, biodegradability, renewability and nontoxicity, polysaccharides are the main part of the naturalbasedsuperabsorbent composites.Graft copolymerization of vinyl monomers onto polysaccharides is an efficient route for the preparation of superabsorbent. Vinyl graft copolymerization onto polysaccharides and proteins is a well known method for synthesis of natural-based superabsorbent composite.[7]

GG is a hydrophilic, nonionic polysaccharide extracted from the endospermic seed of the plant Cyamopsis 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 valuableingredients for foods, cosmetics and pharmaceuticals.[8]

Our previous work, guar gum grafted PMMA superabsorbent nanocomposite was synthesized via free radical graft copolymerization reaction.[9] In this paper we report preparation of superabsorbent composite in presence of potassium per sulphate as an initiator. The synthesized composite showed improved swelling behaviour in presence of potassium per sulphate. According to the initiator concentration, the whole process is optimized and the effect of reaction variables on percentage swelling was studied.

2. Experimental

2.1) Materials

Guar gum (GG, purchased from Shri Ram Gum Industries Basni Jodhpur), Methyl methacrylate (MMA stabilised for synthesis, purchased from Merck), Boric acid (H_3BO_3, purchased from Qualigens Fine Chemicals), Acetone (purchased from Qualigens), Potassium per sulphate (KPS, purchased from Sigma Aldrich) and Ethanol (C_2H_5OH, purchased fromEmsure). All of these are used without further purification and all solutions are prepared in distilled water.

2.2) Method

A series of samples of superabsorbent composite has been prepared by following method. GG (1.5g) was added in 50 mL of distilled water in a round-bottomed flask equipped with stirrer and thermostated water bath. The above solution was stirred for two hours. The monomer MMA (9mL/100mL) was added in above guar gum slurry and mixture was stirred for one an hour. Then required volume of initiator KPS (0.9g/10mL) was added to generate radicals. The aqueous solution of cross-linker boric acid (0.14g/10 mL) was added in the mixture. The reaction mixture was continuously stirred and heated to 60ºC for about two hours. After that it was precipitated using excess of acetone and kept overnight. Then it was washed several times with mixture of distilled water and ethanol (60:40) to remove homopolymer and unreacted mass. The grafted product was dried in oven at 100ºC. Finally, the dried resulting product was pulverized into powder.

2.3) Water Absorbency Measurement

Absorbency of superabsorbent polymers 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 4 hours to reach swelling equilibrium. The swollen gel was taken out, dried between folds of filter paper (blotting method) and weighed. After weighing the swollen samples, the equilibrium water absorbency of the superabsorbent was calculated using Eq. (1)

$$\% \text{ Swelling} = \frac{W_2 - W_1}{W_1} \times 100 \quad \ldots (1)$$

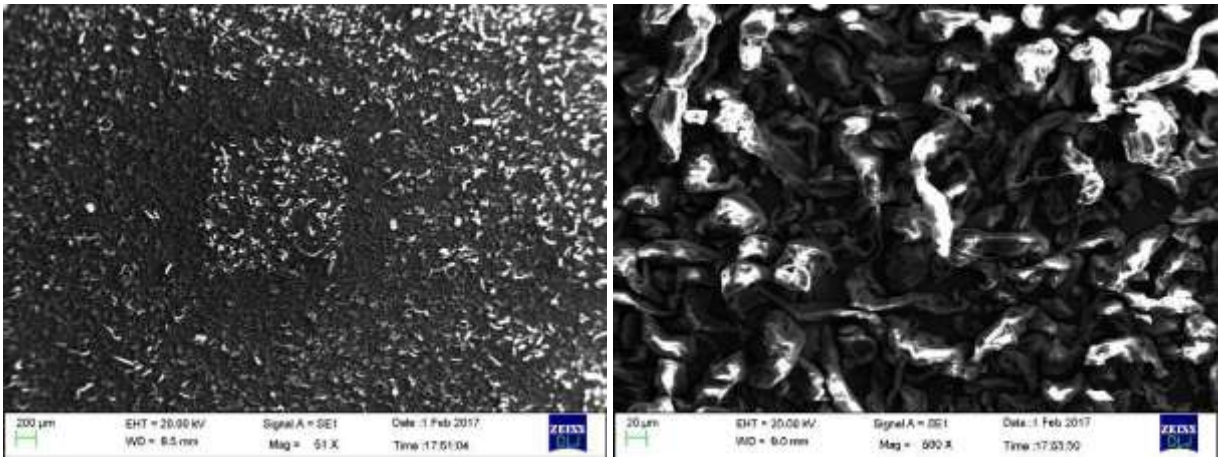
% Swelling is the equilibrium water absorbency of sample which are the averages of three measurements.

W_1 and W_2 are the weight of the dry sample and water swollen sample respectively.

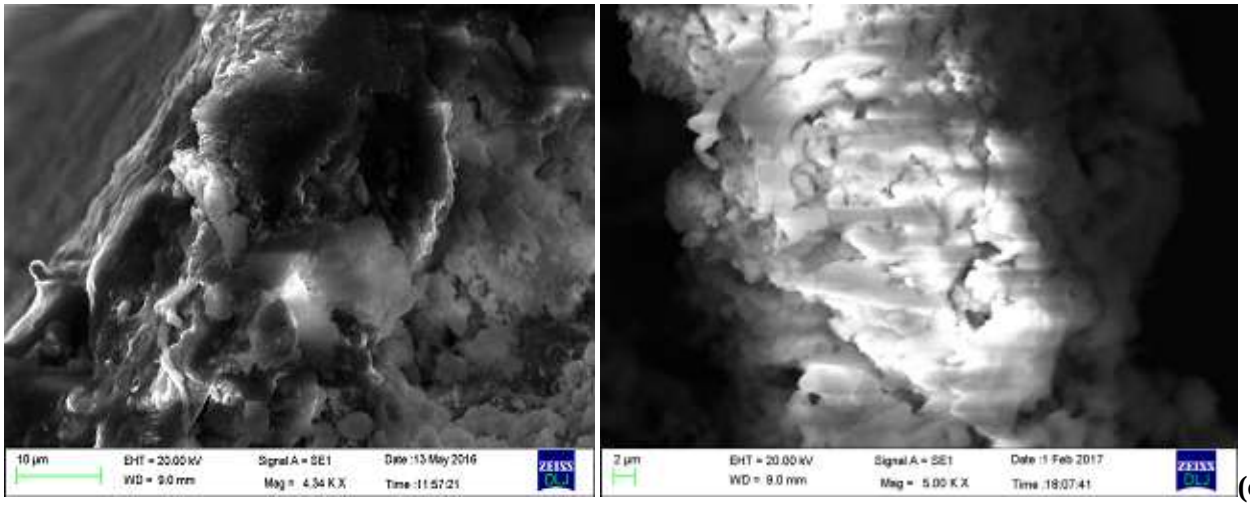
3. Result and discussion

3.1) SEM (Scanning Electron Microscopy)

In order to study surface morphology of prepared superabsorbent composite, SEM analysis of guar gum and grafted composite was carried out using Zeiss instrument. Figure 1 shows SEM micrographs of guar gum and prepared superabsorbent composite at different magnification. It is clear from the figure that superabsorbent has rough surface, porous structure and forming a broad network.The pores in the structure of composite helps in water absorption.



(a) (b)



(c)(d)

Fig.1SEM micrographs of (a) Guar gum (Mag = 51 X) (b) Guar gum (Mag = 500 X) (c) GG grafted PMMA composite (Mag = 4.5KX) (d) GG grafted PMMA composite (Mag = 5 KX)

3.2) FTIR Analysis

FTIR analysis of composite was carried out to study functional groups. FTIR was carried out on sample made by pelleting with KBr. FTIR spectra was collected in Agilent Cray 600 series spectrophotometer in the range 4000-400 cm^{-1}.FTIR spectra of grafted composite shows a broad band in the region between 3440-3520 cm^{-1} which is due to stretching vibration of OH group of guar gum. A peak at 2920 cm^{-1} is because of C-H stretching vibrations. The absorption band at 1680 cm-1 is because of C=O stretching vibrations of PMMA. A peak at 1640 cm^{-1} is due to associated water molecules.The band at 1480 cm^{-1} can be attributed to bending vibrations of C-H bond of $-CH_3$ group. The two bands at 1380 cm^{-1} and 740 cm^{-1} can be attributed to α – methyl group vibrations. The absorption band in the region of 1200-1140 cm^{-1} is due to C-O-C stretching vibrations. The peak at 1020cm^{-1} is due to coupling of C–O stretching and O–H 'in plane' bending vibrations. The presence of such characteristic peaks confirms the grafting of PMMA onto guar gum.

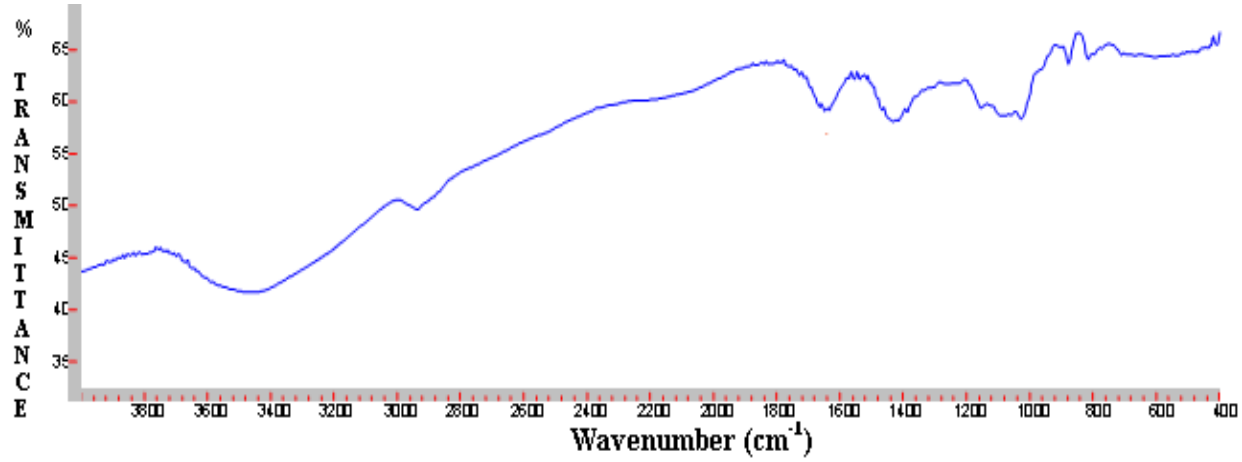


Fig.2FTIR spectra of grafted composite

3.3) XRD (X-ray diffraction) Analysis

XRD analysis of composite was carried out to know its amorphous or crystalline nature.X-ray diffraction (XRD) pattern was obtained with Philips X'pertpyrosystem Cu Kα radiation (λ=1.54 angstrom and theta = 0-80º) at room temperature. The grafted composite shows one prominent peak at scattering angle (2theta) at 26.90º which indicates development of crystallinity in composite. Theaverage crystallite size was calculated using Scherrer equation and found to be 45.4 nm.

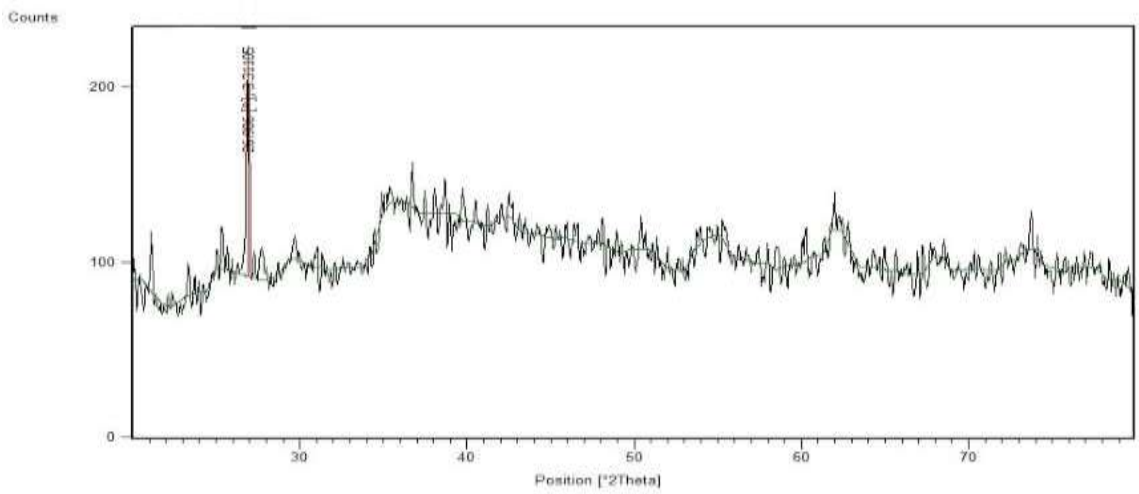


Fig.3 XRD pattern of grafted composite

3.4) Effect of reaction variables

3.4.1) Effect of guar gum concentration

The effect of guar gum concentration on percentage swelling was investigated by preparing a series of superabsorbent composite. The water absorbency increases by increasing guar gum concentration from 1 to 3 % (w/v). On further increase in guar gum content the water absorbency decreases. This is because of the fact that at low guar gum concentration the homopolymerization increases which does not contribute to water absorbency. On increasing guar gum content beyond 3 % (w/v) water absorbency decreases because of decrease in homopolymer content.[10]

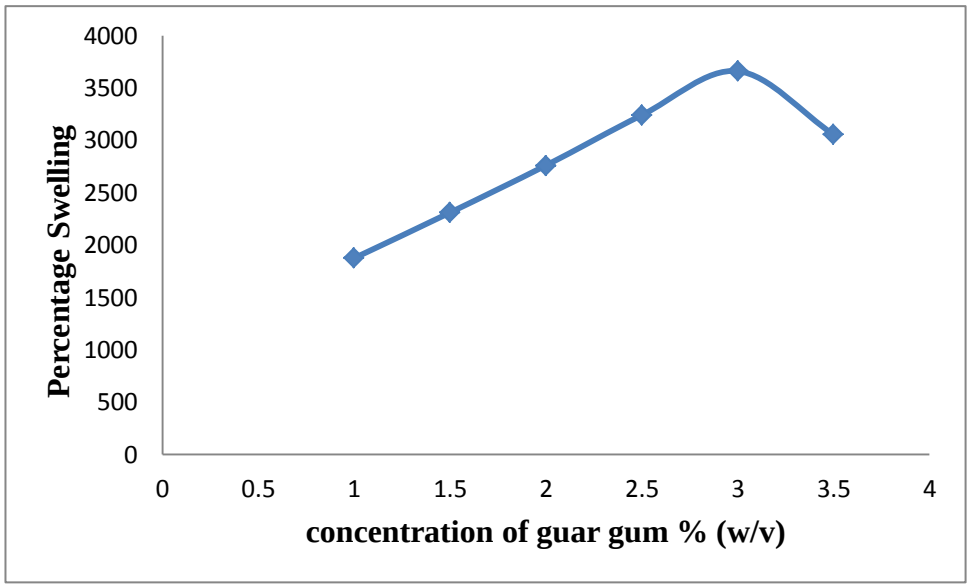


Fig.4 Effect of guar gum concentration on percentage swelling

3.4.2) Effect of monomer concentration

The effect of monomer concentration on percentage swelling was investigated by carrying the concentration of methyl methacrylate and is shown in figure 7. It is clear from the figure that initially water absorbency increases by increasing monomer concentration and reaches maximum at 9 % (v/v) and thereafter it reduces. Co-polymerization between MMA and guar gum increases the percentage swelling thereafter it decreases due to formation of homopolymer of MMA.

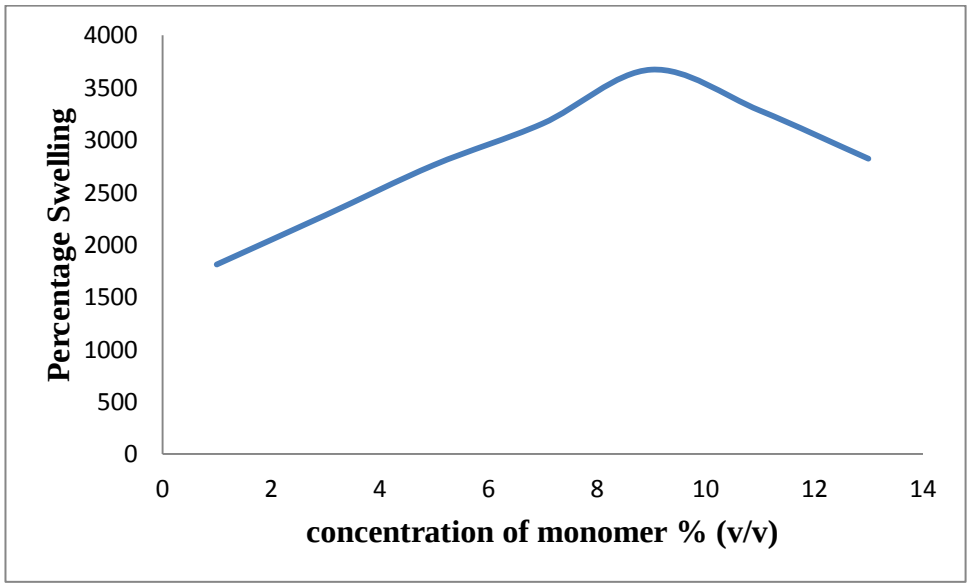


Fig.5 Effect of monomer concentration on percentage swelling

3.4.3) Effect of initiator concentration

The effect of initiator concentration on percentage swelling was studied as shown in figure. The water absorbency increases by increasing potassium per sulphate concentration from 1 to 9 % (w/v). On further increase in initiator content the water absorbency decreases.The initial increment in swelling results from increase in number of active free radical on polysaccharide backbone. The swelling decrease after the maximum may be attributed to increased number of produced radicals led to terminating step via bimolecular collision resulting in enhancedcrosslink density. [7]

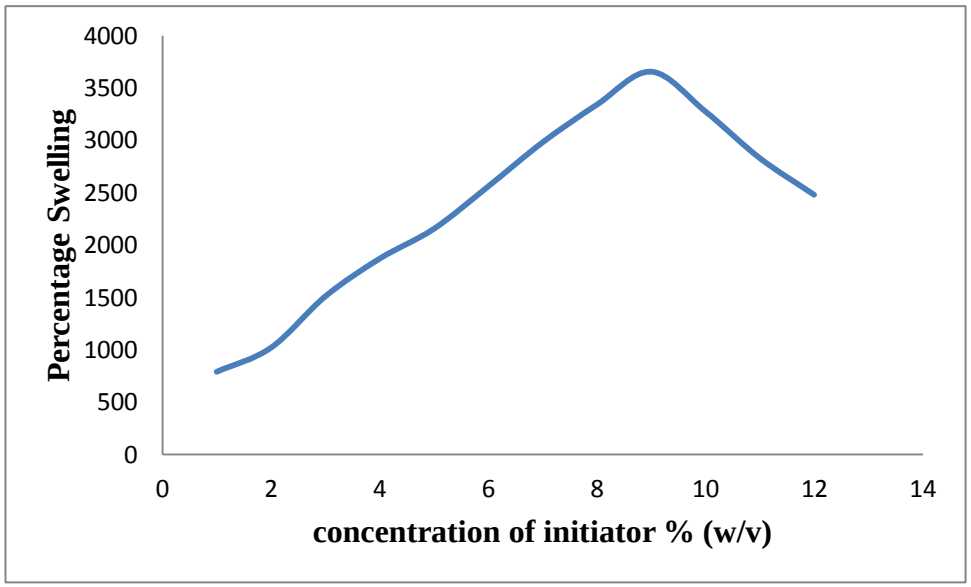


Fig.6 Effect of initiator content on percentage swelling

3.4.4) Effect of cross-linker concentration

The concentration of cross linking agent plays an important role in water absorbency of composite. The percentage swelling of composite decreases by increasing boric acid concentration from 1.4 to 2.2 (w/v) %. This is because of the fact that a high crosslinker concentration will cause the generation of more crosslinking points and the increase of crosslinked density. As a result, the network space left for holding water was minimized and the water absorbency decreased.[11]

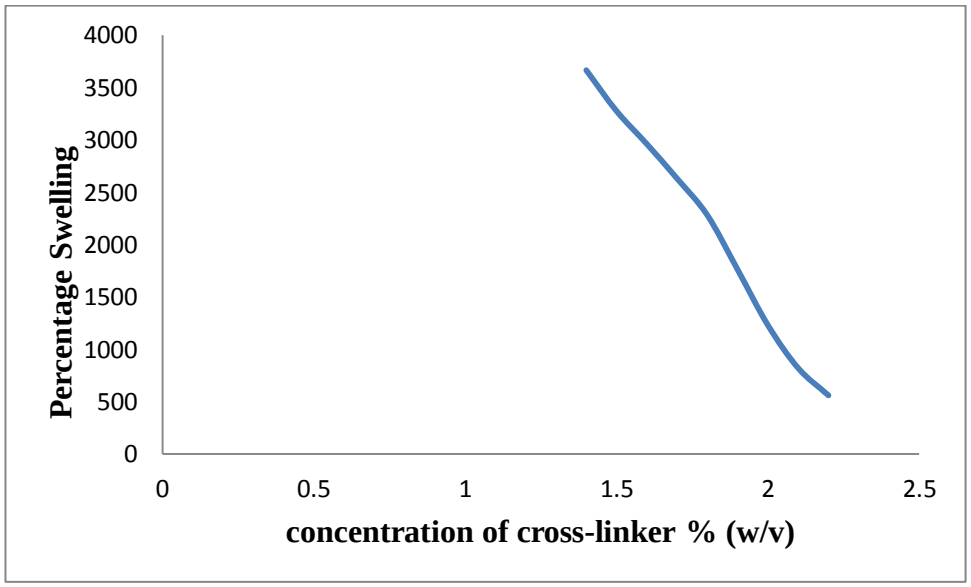


Fig.7 Effect of cross-linking agent on percentage swelling

3.4.5) Effect of pH

In this study, effect of pH on percentage swelling was studied by varying pH from 2 to 13 at room temperature. To prepare pH media, the stock NaOH (pH 13.0)and HCl (pH 2.0) solutions were diluted with distilled water to reach desired basic pH respectively.The percentage swelling of composite increases by increasing pH and reaches maximum at pH 8. After that, percentage swelling decreases by increasing pH beyond 10. In acidic media, most carboxylic acid groups are protonated therefore decreased repulsion of anionic groups leads to a decreased percentage swelling. At higher pH some carboxylate groups are ionized and the

electrostatic repulsion between carboxlate groups causes an enhancement of the swelling capacity. The reason of the swelling loss for the highly basic solutions is the charge screening effect of excess Na^+ in the swelling media, which shield the carboxylate anions and prevent effective anion-anion repulsion.[12]

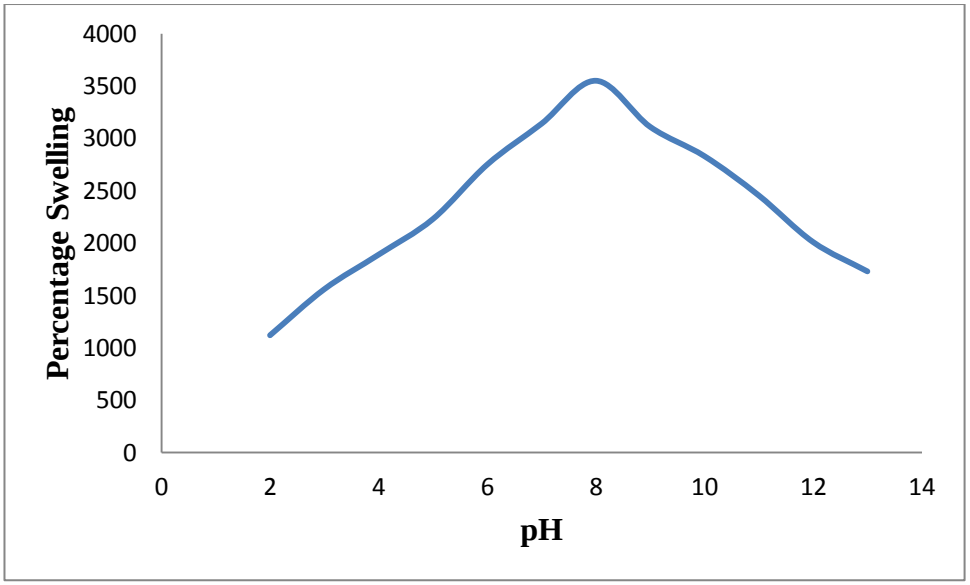


Fig.8 Effect of pH on percentage swelling

3.4.6) Percentage swelling in saline solution

The percentage swelling of composite was also studied in various saline solution. The solution of different concentration of NaCl, CaCl2 and AlCl3 were prepared to study effect of saline environment. The percentage swelling is less than in distilled water. This canbe attributed to change in osmotic pressure inthe environment. The same reason results in thedecrease in swelling as the concentration of saltis increased. At low salt concentration theswelling rate of composite is faster than at higherconcentrations. The factors that caused thewater absorption in the polymer included theosmotic pressure difference between the interiorand exterior of polymer. The increasing osmotic pressure with increase of salt concentration led to decrease in osmotic pressure differencebetween the interior and exterior of the superabsorbent polymer. [13] In addition multivalent cations (Ca^{2+}, Al^{3+}) can neutralize severalcharges inside the gel by complex formation withcarboxylate groups, leading to increased ioniccrosslinking degree and consequently loss of swelling. [14]

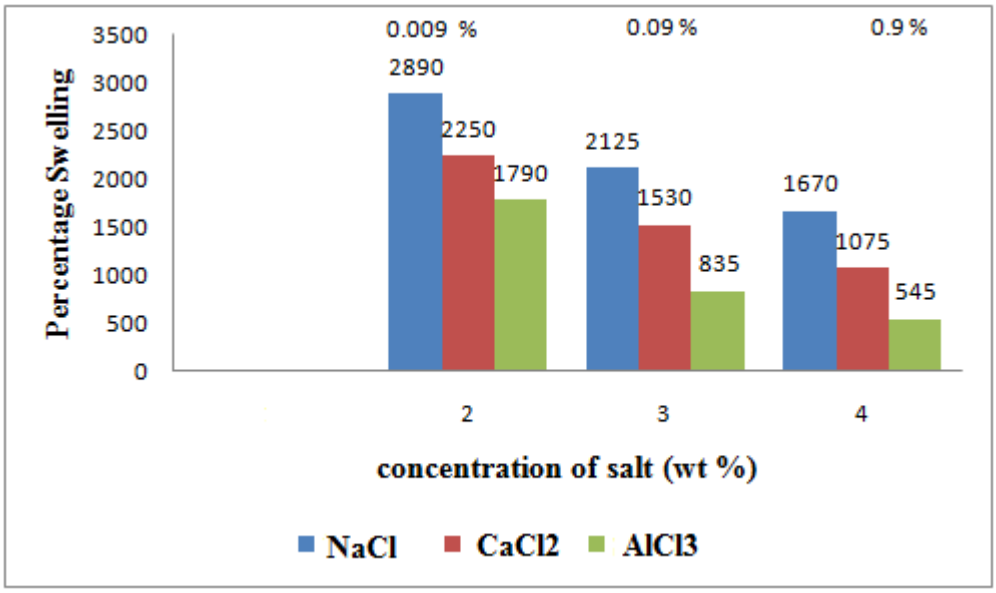


Fig.9 Percentage swelling of composite in various saline solution

4. Conclusion

Novel guar gum-g-poly (methyl methacrylate) superabsorbent composite was synthesized in aqueous solution using potassium per sulphate as an initiator and boric acid as cross-linking agent by free radical graft coplymerization reaction. FTIR confirmed grafting between methyl methacrylate and guar gum. SEM analysis showed that that composite has rough and porous surface. The water absorbency of composite was increased using potassium per sulphate. The composite shows maximum percentage swelling of 3650 % in distilled water and 2890 % in saline solution (NaCl). The effect of reaction variables such as guar gum concentration, monomer concentration, initiator concentration, cross-linker content and pH on percentage swelling was investigated. The water absorption of composite was also studied in various saline solution. The result shows that percentage swelling is decreased by increasing ionic strength of swelling medium. This behavior is because of charge screening effect for monovalent cations as well as ionic crosslinking for multivalent cations. The composite shows good water absorption in pH range of 4-9 which shows its potential to be used in areas such as agriculture, horticulture etc.

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