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# Preparation of poly(acrylamide-co-acrylic acid)-grafted gum and its flocculation and biodegradation studies

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ABSTRACT

Biodegradation studies of Gum ghatti (Gg) and acrylamide-co-acrylic acid based flocculants [Gg-cl-poly(AAm-co-AA)] have been reported using the soil composting method. Gg-cl-poly(AAm-co-AA) was found to degrade 89.76% within 60 days. The progress of biodegradation at each stage was monitored through FT-IR and SEM. Polymer was synthesized under pressure using potassium persulphate-ascorbic acid as a redox initiator and N,N′-methylene-bis-acrylamide as a crosslinker. Synthesized polymer was found to show pH, temperature and ionic strength of the cations dependent swelling behavior. Gg-cl-poly(AAm-co-AA) was utilized for the selective absorption of saline from different petroleum fraction-saline emulsions. The flocculation efficiency of the polymer was studied as a function of polymer dose, temperature and pH of the solution. Gg-cl-poly(AAm-co-AA) showed maximum flocculation efficiency with 20 mol $L^{-1}$ polymer dose in acidic medium at 50 °C.



## 1. Introduction

Synthetic and natural polymers along with their composites and blends are gathering more and more attraction and used in different applications because of their low cost, easy availability and ability to modify their properties conveniently for a particular application. But synthetic polymers produces a lot of non-biodegradable solid waste which causes environmental pollution. Therefore, there is an increasing demand of biodegradable polymeric materials as a replacement of the synthetic polymers and solution of the solid waste management. Biodegradation is an alternative, quick and very efficient way to reduce or degrade the solid plastic waste without polluting the environment. It is the enzymatic or chemical decomposition of the polymeric materials in association with microorganisms or their secretion products (Abrusci, Marquina, & Catalina, 2007; Lesinsky, Fritz, & Braun, 2004; Shimao, 2001). Therefore, biodegradable plastics may be defined as those in which a significant change in chemical structure is observed under specific environmental conditions. Biodegradation brings about the fragmentation of the polymers and convert them into lower molecular weight compounds. It depends on the several factors like chemical and physical properties of the polymers, constitution of the final product, length and crystallinity of the polymer chain (Nageotte, Pester, Pradet, & Bayard, 2006). Properties and conditions of the test system also influence the biodegradability of the polymers. Generally, most vulnerable components of the biodegradable polymers are derived from the natural renewable resources like cellulose, starch, soy protein and gums (Araújo, Cunha, & Mota, 2009; Ashori, 2008; Chen, Li, & Ren, 2011; Liua, Misra, Askelanda, Drzala, & Mohanty, 2005; Prashanth, Lakshman, Shamala, & Tharanathan, 2005). Biodegradable polymers have a number of applications in different areas like drug delivery systems, gene therapy, soft-tissue engineering and biomedical (Mohanty, Wibowo, Misra, & Drzal, 2004; Moller, Weisser, Bischoff, & Schnabelrauch, 2007; Shibata, Cao, & Fukumoto, 2008; Sun, Song, & Zheng, 2007; Tiwari, Grailer, Pilla, Steeber, & Gong, 2009).

Flocculation is the process of removal of organic and inorganic impurities from the contaminated water by converting the suspended or colloidal particles into larger flocs and separating them from the water (Ghosh, Sen, Jha, & Pal, 2010). Flocculent materials are basically of two types; organic and inorganic flocculants. The separation of the flocs produced by the inorganic flocculants is very difficult because they are fragile and have low share resistance. Therefore, biodegradable polysaccharide based flocculants are preferred because they are free from the above-mentioned drawbacks. Moreover, they have additional advantages of low cost, abundant availability and design versatility (Ghimici & Nichifor, 2010). Flocculation efficiency depends upon the nature of functional groups,

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charge density and the molar mass of the polymer alongwith the pH, temperature and ionic strength of the medium. Efficiency of the synthetic flocculants is much better than the natural ones but they are non-biodegradable. In the past few years a lot of research work have been reported on the chemical modification of biodegradable polysaccharides (guar gum, gum xanthan, teramid kernel, chitosan, etc.) which have advantages of both synthetic and natural polymers (Abdel-Halim & Al-Deyab, 2011; Ghimici & Nichifor, 2010; Ghorai, Sinhamahpatra, Sarkar, Panda, & Pal, 2012).

In this research paper we have reported the biodegradation studies and flocculation behavior of Gum ghatti and acrylamide-co-acrylic acid based hydrogels. Biodegradation studies were done using soil composting method and the progress was monitored at each stage of degradation. Effect of pH, temperature and ionic strength of different cations on the swelling behavior was also investigated. Moreover, hydrogel was utilized for the selective removal of saline from different petroleum fraction-saline emulsions. The flocculation characteristics of the hydrogel were studied w.r.t. polymer dose, temperature and pH.

## 2. Experimental

### 2.1. Materials

Acrylamide (AAm), acrylic acid (AA) Gum ghatti (Gg), N,N′-methylene-bis-acrylamide (MBA), potassium persulphate (KPS), ascorbic acid (ABC), petroleum ether and kaolin were purchased from Merck and used as received. Petrol and diesel were purchased from Indian Oil Corporation Limited. All the chemicals were of analytical grade and used without further purification. Flocculation studies were done on Micro 1000 IR Turbidimeter (HF Scientific Incorporation).

### 2.2. Methods

#### 2.2.1. Instrumental analysis

FTIR spectra of the polymer and the samples at different stages of biodegradation were taken on PERKIN ELMER RXI spectrophotometer using KBr pellets (Sigma–Aldrich). Scanning electron micrographs of the samples were taken on LEO, 435VF, LEO Electron Microscopy Ltd. TGA/DTA/DTG studies of Gg and Gg-cl-poly(AAm-co-AA) were done on TG/DTA 6300, SII EXSTAR 6000 in-air at a heating rate of 10 °C per minute. Approximately 5–10 mg of the samples were placed in the platinum crucible and placed in the furnace of thermal analyzer for analysis.

#### 2.2.2. Synthesis of flocculants

For each experiment Gg solution was prepared by adding Gg (1.0 g) into 10 ml of triple distilled water in the reaction flask with constant stirring followed by the addition of AAm (0.7042 mol $L^{-1}$), AA (8.694 mol $L^{-1}$) and MBA (0.0811 mol $L^{-1}$) in the reaction mixture with continuous stirring. A mixture of KPS and ABC in 1:1 molar ration was added into the reaction mixture to initiate the polymerization reaction. The reaction vessel was placed in the autoclave and the reaction was carried-out at 9 psi. After 3 h the reaction was stopped and the product was soxhlet extracted for 3–4 h with acetone and for the removal of homopolymer. Synthesized polymer was dried in hot air oven at 50 °C till a constant weight was obtained.

#### 2.2.3. Swelling studies in deionized water

Swelling studies of Gg-cl-poly(AAm-co-AA) in deionized water was carried-out at different time intervals (4, 8, 12, 16, 20 and 24 h), varied temperatures (30, 40, 50, 60 and 70 °C) and pH (3.0–13.0) in deionized water. 100 mg of the each sample was immersed in 100 ml deionized water. After a definite time interval sample was taken out, gently wiped and weighed. Percentage swelling ($P_s$) was calculated by using Eq. (1) (Kaith, Jindal, Mittal, & Kumar, 2012):

$$P_s = \frac{W_s - W_d}{W_d} \times 100 \quad (1)$$

where $W_s$ and $W_d$ are the weights of the swelled and dry polymers, respectively.

After the optimization of time for maximum $P_s$, effect of temperature on $P_s$ was studied at pre-optimized time followed by the optimization of pH for maximum $P_s$ at pre-optimized time and temperature.

#### 2.2.4. Swelling studies in different salt solutions

Effect of ionic strength of different cations such as $Na^+$, $Ba^{2+}$, $Fe^{3+}$ and $Sn^{4+}$ with different ionic strengths (0.01, 0.02, 0.03, 0.04 and 0.05 mol $L^{-1}$) on the $P_s$ of Gg-cl-poly(AAm-co-AA) was investigated in NaCl, $BaCl_2$, $FeCl_3$ and $SnCl_4$ salt solutions, respectively at pre-optimized time, temperature and pH in deionized water. 100 mg of the polymer samples were added in the respective salt solutions already kept at pre-optimized temperature. After 16 h the samples were taken-out, wiped gently to remove the excess water on the surface and weighed carefully. $P_s$ was calculated as per Eq. (1).

#### 2.2.5. Selective absorption of saline from different petroleum fraction-saline emulsions

1% NaCl solution was used as saline and the different petroleum fractions taken were kerosene, diesel, petrol and petroleum ether. Different emulsions of petroleum fractions and saline were prepared by adding 50 ml of each saline and petroleum fraction in a 250 ml conical flask. 10 ml of tween-20 was added to the conical flask for the preparation of stable emulsion. The flask was shacked in an automatic shaking machine (LABCO, India) and after the preparation of a stable emulsion 100 mg of the polymer was added into every emulsion, i.e. petrol-saline, kerosene-saline, diesel-saline and petroleum ether-saline emulsions. Saline uptake studies were done at pre-optimized time, temperature and pH in de-ionized water. After pre-optimized time the flasks were taken out of the shaker and placed undisturbed for 48 h to break the emulsion. After 48 h the petroleum fraction was separated from the flask by using a separating funnel and the unabsorbed saline content left after the absorption was measured.

#### 2.2.6. Biodegradation studies

Biodegradable behavior of Gg-cl-poly(AAm-co-AA) was studied by using soil composting method (Kaith, Jindal, Maiti, & Jana 2010). Rectangular samples of the dimensions 2 cm × 2 cm × 1.5 cm were prepared and buried in the compost collected from the waste water effluent discharge plant of the National Institute of Technology, Jalandhar, India. Samples were buried in the compost at 2 cm depth and the distance between each sample was 3 cm. The microbial rich water of the treatment plant was regularly fed at every alternate day to overcome the water loss by evaporation. Samples were taken out from the compost after a regular time interval of 5 days, cleaned properly and weighed. The progress of degradation at each stage was monitored through SEM and FTIR.

The percentage weight loss after particular time interval was determined as follows (Kaur, Bhalla, Deepika, & Gautam, 2009):

$$\text{Weight loss } (\%) = \frac{W_i - W_r}{W_i} \times 100 \quad (2)$$

where $W_i$ is the initial weight of the sample and $W_r$ is the weight after 5 days.

#### 2.2.7. Flocculation studies

Flocculation studies were done using Standard Test Jar (Jha, Agarwal, Mishra, & Rai, 2001). Initially, the instrument was

calibrated with the standard solutions (0.02, 10, 100 and 1750 NTU). 50 ppm kaolin suspension was used as the turbid solution. 500 ml of kaolin solution was added in a 1000 ml beaker equipped with a variable speed agitator (0–250 rpm). The agitator was adjusted at 180 rpm for 10 min. Initially, blank reading was taken followed by the addition of polymer to the kaolin suspension. Readings were taken after every 10 min till almost constant turbidity was obtained. Different doses of the polymer were used in order to get the optimum dose level for maximum flocculation capacity. Further the flocculation temperature was optimized followed by the optimization of pH.

## 3. Results and discussion

### 3.1. Thermogravimetric analysis, differential thermal analysis and differential thermo-gravimetric analysis (TGA/DTA/DTG) studies

TGA of Gg and Gg-cl-poly(AAm-co-AA) have been studied as a function of percentage weight loss vs. temperature at a heating rate of 10 °C/min in-air. DTA is studied as a function of energy loss vs. temperature and DTG is studied as a function of rate of weight loss vs. time. The analysis was performed in order to examine the changes in thermal properties of the Gg brought about by graft copolymerization with AAm-co-AA and crosslinking with MBA under pressure.

In the TGA of Gg-cl-poly(AAm-co-AA), initial decomposition temperature (IDT) was observed at 164.1 °C, whereas final decomposition temperature (FDT) was observed at 560.9 °C. IDT of the grafted polymer was found to be lower than that of Gg (206.9 °C) (Kaith, Jindal, Mittal, & Kumar, 2012), whereas, FDT was found to be higher than that of Gg (521.6 °C). Lower IDT of grafted polymer may be due to the formation of imide group with the evolution of ammonia during the grafting of poly(AAm-co-AA) chains onto Gg backbone (Behari, Pandey, Kumar, & Taunk, 2001). In TGA of Gg two stage decomposition was observed in the temperature range of 206.9–331.4 °C with 46.6% weight loss and 331.4–521.6 °C with 31.2% weight loss (Kaith, Jindal, Mittal, & Kumar, 2012), however, TGA of Gg-cl-poly(AAm-co-AA) showed decompositions in the temperature range of 164.1–436–9 °C with 56.2% weight loss and 436.9–560.9 °C with 26.1% weight loss (Table 1). DTG of Gg showed the maximum decomposition at 479.0 °C with 2.23 mg/min weight loss (Kaith, Jindal, Mittal, & Kumar, 2012), whereas, DTG of Gg-cl-poly(AAm-co-AA) showed the maximum decomposition at 558.9 °C with 0.647 mg/min rate of weight loss (Table 1). Thus, it is observed from the DTG studies that the rate of weight loss was higher in case of Gg than Gg-cl-poly(AAm-co-AA). DTA of Gg showed two exothermic peaks at 483.2 and 492.7 °C whereas, Gg-cl-poly(AAm-co-AA) showed exothermic peaks at 534.7 and 559.5 °C. In Gg DTG peaks were observed at lower temperature than Gg-cl-poly(AAm-co-AA). Therefore, from the thermal studies it is confirmed that the thermal stability of Gg got enhanced after grafting and crosslinking. This enhanced thermal stability of the grafted polymer may be due to the formation of crosslinks between different polymeric chains through covalent bonding.

### 3.2. Swelling studies Gg-cl-poly(AAm-co-AA) in deionized water

#### 3.2.1. Effect of time on $P_s$

Effect of swelling time on $P_s$ was studied at different time intervals (4, 8, 12, 16, 20 and 24 h) (Fig. 1a). From the figure it is observed that initially $P_s$ increases with increasing swelling time and attains the maximum value (1284%) after 16 h. Whereas, further increase in swelling time result in no further increase in $P_s$. This may be due to the fact that with increase in time interval, porous network of polymer become fully saturated with no more accommodation for the solvent molecules.

#### 3.2.2. Effect of temperature on $P_s$

Effect of temperature on $P_s$ was observed at different temperatures (30, 40, 50, 60 and 70 °C) and pre-optimized time (Fig. 1b). Initially, $P_s$ increases with increase in temperature up to 60 °C with maximum value of 1418%. However, a remarkable decrease in $P_s$ was observed with further increase in temperature. This may be because of the fact that initially with the increase in temperature the elasticity of the polymeric matrix increases resulting in the larger $P_s$ but after reaching optimum temperature matrix collapses and lead to desorption with further increase in $P_s$.

#### 3.2.3. Effect of pH on $P_s$

Effect of pH on the $P_s$ was observed in the solutions of pH ranging from 3.0 to 13.0 at pre-optimized time and temperature (Fig. 1c). pH of the different solutions was maintained by using 1 N HCl and 1 N NaOH solutions. In the solutions of pH 3.0, 4.0, 5.0 and 6.0 the value of $P_s$ was found to be 368.42, 442.85, 633.76 and 793.65%, respectively. In the neutral medium the value of $P_s$ increases and attains a maximum value of $P_s$ (1418%), whereas, in the solutions of alkaline of pH 8.0, 9.0, 10.0, 11.0, 12.0 and 13.0 the value $P_s$ decreases, i.e. 927.58%, 752.94%, 677.35%, 575%, 464.17% and 333.92%, respectively. Extent of swelling in dilute electrolyte solutions largely depends on the osmotic swelling pressure ($\pi_{ion}$), which is given as (Bajpai, 1999):

$$\pi_{ion} = RT\Sigma(C_i^g - C_i^s) \quad (3)$$

where $C_i^g$ and $C_i^s$ are the molar concentrations of mobile ions in the swollen gel and external solution, respectively. $R$ is gas constant and $T$ is the absolute temperature.

In the neutral medium, the concentration of mobile ions ($C_i^s$) in the swelling medium becomes very small and the value of $\pi_{ions}$ becomes very large resulting in the enhanced swelling. Whereas, in the acidic solutions most of the carboxylate ions get protonated (Mahdavinia, Pourjavadi, Hosseizadeh, & Zohurian, 2004) and the value of ions within the swollen gel ($C_i^g$) decreases leading to the reduced value of $\pi_{ions}$. On the other hand, in alkaline pH —COOH groups completely dissociate but at the same time the concentration of $Na^+$ and $OH^-$ ions is very high which reduces the value of $\pi_{ions}$ and $P_s$.

**Table 1**
TGA/DTA/DTG of Gg and Gg-cl-poly(AAm-co-AA).

| Sample | TGA | | | | DTA | | DTG | |
|---|---|---|---|---|---|---|---|---|
| | IDT (°C) | 1st stage decomposition, °C (%wt. loss) | 2nd stage decomposition, °C (%wt. loss) | FDT (°C) | Exothermic peaks at different decomposition temperature (μV) | | Decomposition temperature, °C (rate of wt. loss in mg/min) | |
| | | | | | 1st (°C) | 2nd (°C) | 1st (°C) | 2nd (°C) |
| Gg | 206.9 | 206.9–331.4 (46.6%) | 331.4–521.6 (31.2%) | 521.6 | 483.2 (230) | 492.7 (154) | 299.1 (1.463) | 479.0 (2.230) |
| Gg-cl-poly(AAm-co-AA) | 164.1 | 164.1–436.9 (56.2) | 436.9–560.9 (38.1) | 560.9 | 534.7 (77.0) | 559.5 (89.1) | 374.9 (0.654) | 558.7 (0.647) |

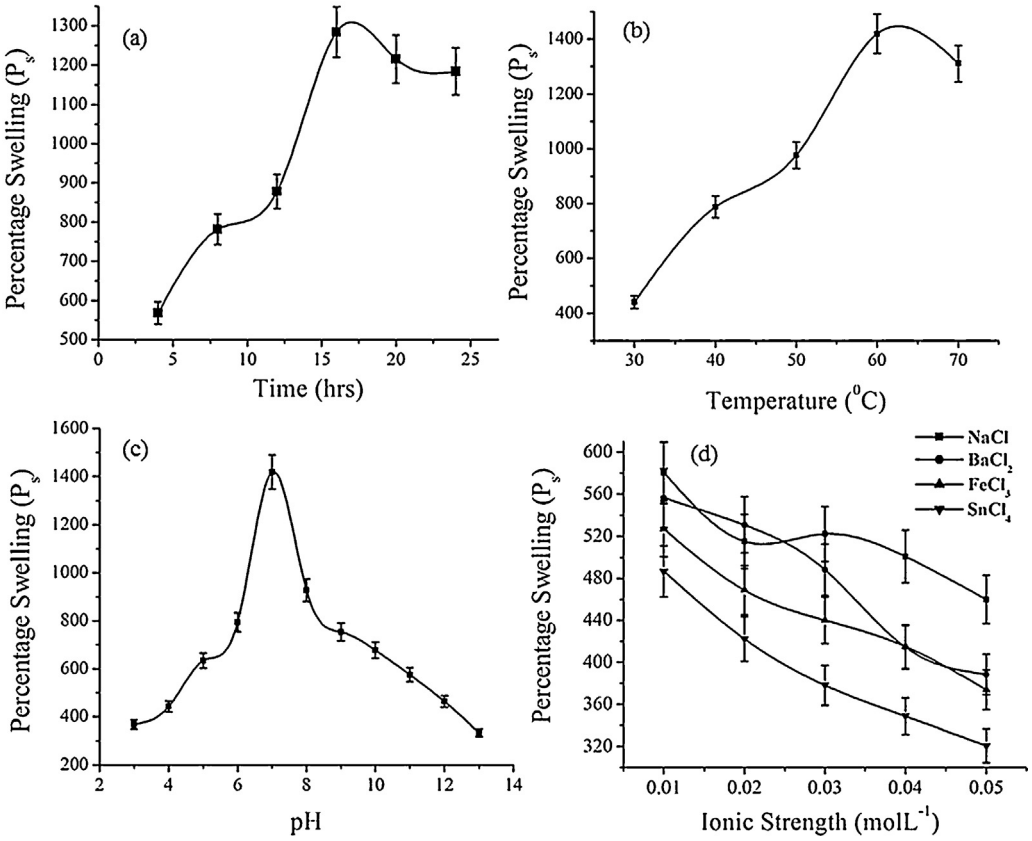



**Fig. 1.** (a) Effect of time on $P_s$ of Gg-cl-poly(AAm-co-AA); (b) effect of temperature $P_s$ of Gg-cl-poly(AAm-co-AA); (c) effect of pH on $P_s$ of Gg-cl-poly(AAm-co-AA); and (d) effect of ionic strength of various cations on $P_s$ in different salt solutions.

### 3.2.4. *Effect of ionic strength of different cations on $P_s$*

Fig. 1d reveals the effect of ionic strength of different cations on $P_s$ of Gg-cl-poly(AAm-co-AA). From the figure it is observed that $P_s$ decreases with increase in the ionic strength of the cations in the respective salt solutions. Smaller value of $P_s$ with increased ionic strength of the cations may be due to reverse osmosis process. Moreover, the value of $\pi_{ions}$ decreases with an increase in the molar concentration of counter ions in the external solution which ultimately reduces the swelling capacity and $P_s$. Further the value of $P_s$ decreases with increasing ionic charge of the metal cation because the carboxylate groups of the polymer form complexes with the cations and reduces the swelling. Therefore, a reduced value of $P_s$ was observed with the increased cationic charge (Pourjavadi & Mahdavinia, 2006).

## 3.3. *Selective removal of saline from different petroleum fraction-saline emulsions*

Initially the absorption behavior of the polymer in pure petroleum fractions was checked and it was observed that the polymer do any absorb any of the petroleum fractions studied, i.e. petrol, kerosene, diesel and petroleum ether. Selective removal of saline from different emulsions was studied at the pre-optimized time (16 h), temperature (60 °C) and pH (7.0) in deionized water. Table 2 shows the percentage removal of saline from kerosene-saline, diesel-saline, petrol-saline and petroleum ether-saline emulsions by Gg-cl-poly(AAm-co-AA). Maximum percentage removal of 35.5%, 26.5%, 39.0% and 42.0% was observed in kerosene-saline, diesel-saline, petrol-saline and petroleum ether-saline emulsions, respectively. Gg-cl-poly(AAm-co-AA) was found to follow the trend of saline removal in the order petroleum ether-saline > petrol-saline > kerosene-saline > diesel-saline. The reason for this type of trend may be the number of hydrocarbon groups present in the polymer fraction, larger the number of hydrocarbon groups more will be the hydrophobic character and lesser the absorption of saline leading to lesser percentage swelling. Since, number of carbon atoms in petroleum ether is the least (C < 12), followed by petrol ($C_4$–$C_8$), kerosene ($C_{10}$–$C_{15}$) and diesel (C > 15).

## 3.4. *Flocculation characterization of Gg-cl-poly(AAm-co-AA)*

### 3.4.1. *Effect of polymer dose on flocculation efficiency*

Fig. 2a shows the effect of polymer dose on the flocculation efficiency of Gg-cl-poly(AAm-co-AA) in highly turbid kaolin

**Table 2**
Percentage removal of saline from different petroleum fraction-saline emulsions.

| Sample | Percentage saline removal | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Kerosene-saline | | | Diesel-saline | | | Petrol-saline | | | Pet. ether-saline | | |
| | % removal | ±SD | ±SE | % removal | ±SD | ±SE | % removal | ±SD | ±SE | % removal | ±SD | ±SE |
| Gg-cl-poly(AAm-co-AA) | 35.5 | 1.11 | 0.64 | 26.5 | 0.52 | 0.30 | 39.0 | 1.38 | 0.80 | 42.0 | 0.52 | 0.30 |

whereas, no. of replications = 03; amount of each emulsion taken = 100 ml (1:1, v/v); weight of superabsorbent taken for each emulsion = 1.0 g.

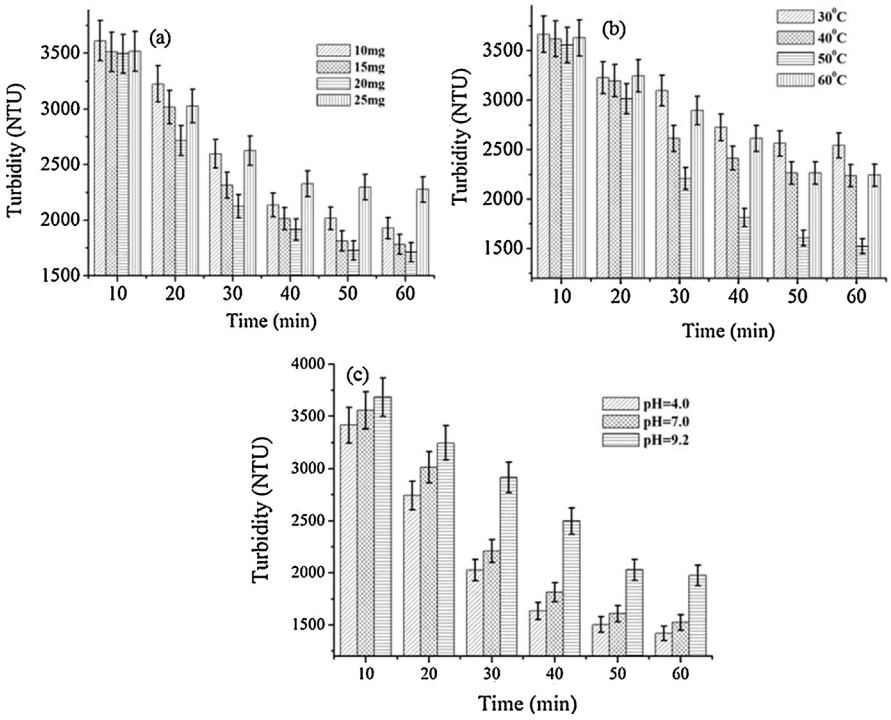



**Fig. 2.** (a) Effect of time on turbidity; (b) effect of temperature on turbidity; and (c) effect of pH on turbidity.

suspension. Initially flocculation efficiency was found to increase with increase in polymer does and minimum turbidity of 1711.13 NTU was observed with 20 mg $L^{-1}$ polymer dose. However, lesser flocculation efficiency was observed with further increase in polymer dose. The initial increase in flocculation efficiency with increase in polymer dose may be due to the formation of particle–polymer–particle complex where polymer acts as a bridge between different suspended particles (Tian & Xie, 2008). When the suspended kaolin particles come in contact with the polymer network some of them get adsorbed on the surface of the polymer and form an extended polymer chain. Now, when other particles comes in contact with the extended polymer chain they also get attached with the remaining free functional groups on the polymer chain and form a complex where polymer acts as bridge between different kaolin particles. However, above the optimum polymer dose the particles will envelope between different polymer chains and will not come in contact with the functional groups of the polymer (Xie, Feng, Cao, Xia, & Lu, 2007). The solution will be re-stabilized and a higher value of turbidity will be observed. Therefore, at too higher polymer dose the formation of particle–polymer–particle complex will not take place resulting in decreased flocculation efficiency.

### 3.4.2. *Effect of temperature on flocculation efficiency*

Fig. 2b reveals the effect of temperature on flocculation efficiency of Gg-cl-poly(AAm-co-AA). It is observed that initially flocculation efficiency increases with increase in temperature and attains the minimum value of turbidity (1523.42 NTU) at 50 °C. The initial increase in temperature supports the particle–polymer–particle complex and reduces the value of turbidity or increases the flocculation efficiency. However, further increase in temperature increases the value of turbidity. It may be because of the fact that at higher temperatures the kinetic energy of polymer molecules will increase and the kaolin particles will redisperse resulting in the higher value of turbidity or lesser flocculation efficiency.

### 3.4.3. *Effect of pH on flocculation efficiency*

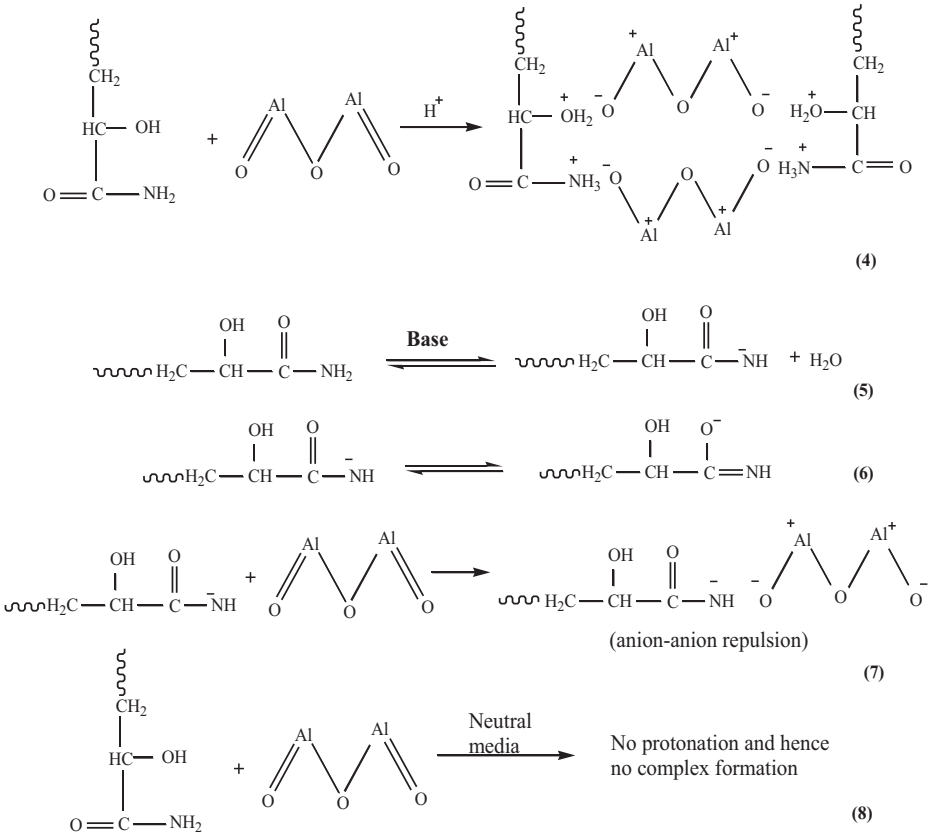
Effect of pH on the flocculation efficiency of Gg-cl-poly(AAm-co-AA) was examined at pre-optimized polymer dose and temperature (Fig. 2c). The proposed mechanism of the flocculation behavior of Gg-cl-poly(AAm-co-AA) at different pH is shown in Scheme 1. It is observed from the figure that the maximum flocculation efficiency was observed in acidic medium. Under acidic conditions the hydroxyl and amide groups of the polymer network will be protonated and give overall a cationic charge to the polymer structure (Eq. (4), Scheme 1). The negatively charged kaolin particles will attach to these cationic sites (Eq. (4), Scheme 1) and form larger flocs. Whereas, under alkaline conditions amides are weakly acidic and resonance stabilized (Eqs. (5) and (6), Scheme 1). The anionic repulsion between the polymer and the kaolin particles will decrease the flocculation efficiency or increase the turbidity. In case of neutral medium, the protonation of free amide and hydroxyl groups will not take place and no complex formation will be observed (Eq. (8), Scheme 1).

### 3.5. *Biodegradation studies of Gg-cl-poly(AAm-co-AA)*

In the crosslinked network of Gg-cl-poly(AAm-co-AA), the process of biodegradation starts at Gg backbone as polysaccharides are well known for their biodegradable nature. The progress of biodegradation was monitored regularly after a time interval of 5 days and the results are compiled in Table 3. The process of

**Table 3**
Biodegradation studies of Gg and Gg-cl-poly(AAm-co-AA).

| Sample Code | Percentage weight loss at different time intervals (days) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 5 | 10 | 15 | 20 | 25 | 30 | 35 | 40 | 45 | 50 | 55 | 60 |
| Gg-cl-poly(AAm-co-AA) | 13.33 | 21.95 | 34.92 | 46.06 | 49.47 | 54.36 | 58.43 | 69.53 | 72.68 | 76.86 | 84.43 | 89.76 |




**Scheme 1.** Mechanism of flocculation of Gg-cl-poly(AAm-co-AA) at different pH.

biodegradation of Gg-cl-poly(AAm-co-AA) was found to be continuous and the percentage weight loss was found to increase with increasing number of days. Gg-cl-poly(AAm-co-AA) was found to degrade up to 89.76% within a time interval of 60 days. The degradation of polymer samples may be due to the enzymatic and chemical degradation. Moreover, in the microbe rich composting media the secretion products of the microbes attack the samples and cause the cleavage of chemical bonds leading to bacterial degradation (Kaith, Jindal, Maiti, & Jana, 2010).

### 3.5.1. Evidences of biodegradability

*3.5.1.1. FT-IR.* FT-IR spectra of Gg-cl-poly(AAm-co-AA) and at different stages of biodegradation were recorded (Fig. 3a–d). The FT-IR of Gg-cl-poly(AAm-co-AA) showed peaks at 2934.6 $cm^{-1}$ (—OH stretching of AA), 1717.5 $cm^{-1}$ (C=O stretching of amide I band), 1454.9 $cm^{-1}$ (NH in plane bending of amide II band), 1245.9 and 1166.0 $cm^{-1}$ (CN stretching vibrations of amide III band), 512.9 $cm^{-1}$ (OCN deformations of amide IV band) in addition to the peaks obtained in the FTIR of Gg (Kaith, Jindal, Mittal, & Kumar, 2012). Degraded samples of Gg-cl-poly(AAm-co-AA) show variation in the peaks as compare to the FTIR peaks obtained in the spectrum of crosslinked polymer before degradation. The intensity of the peaks initially observed at 1454.9 $cm^{-1}$, 1245.9 $cm^{-}$ and 1166.0 $cm^{-1}$ was found decreased at biodegradation stage-I due to the starting of breaking down of the crosslinked network. However, degradation of individual compounds like Gg, poly(AAm-co-AA) and MBA started in the biodegradation stage-II. In this stage, the degradation of Gg is the major process and shifting or complete disappearance of the peaks related to Gg was prominent. In the third and final stage of biodegradation most of the FTIR peaks initially observed in the FT-IR spectrum of Gg-cl-poly(AAm-co-AA) were completely shifted or disappeared. Thus, FT-IR

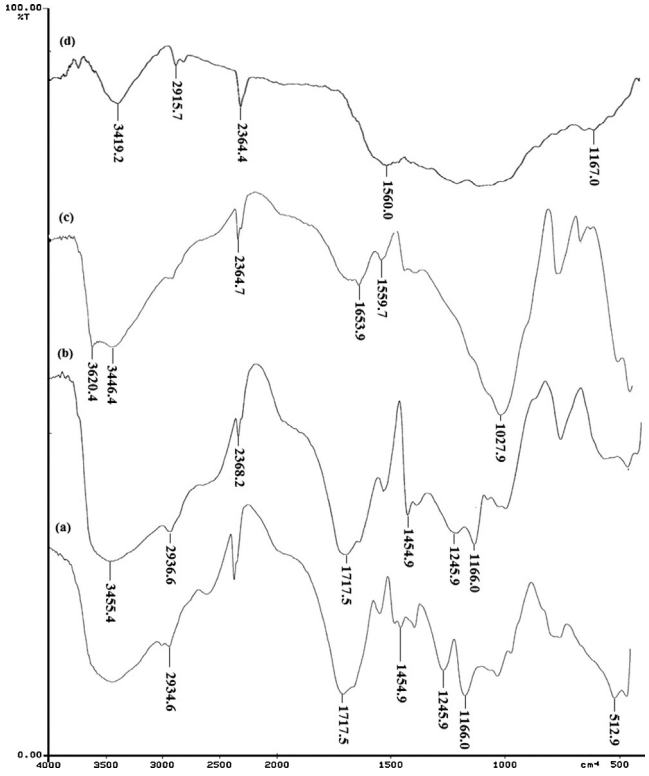



**Fig. 3.** FT-IRs of (a) Gg-cl-poly(AAm-co-AA); (b) biodegradation stage-I of Gg-cl-poly(AAm-co-AA); (c) biodegradation stage-II Gg-cl-poly(AAm-co-AA); and (d) biodegradation stage-III of Gg-cl-poly(AAm-co-AA).

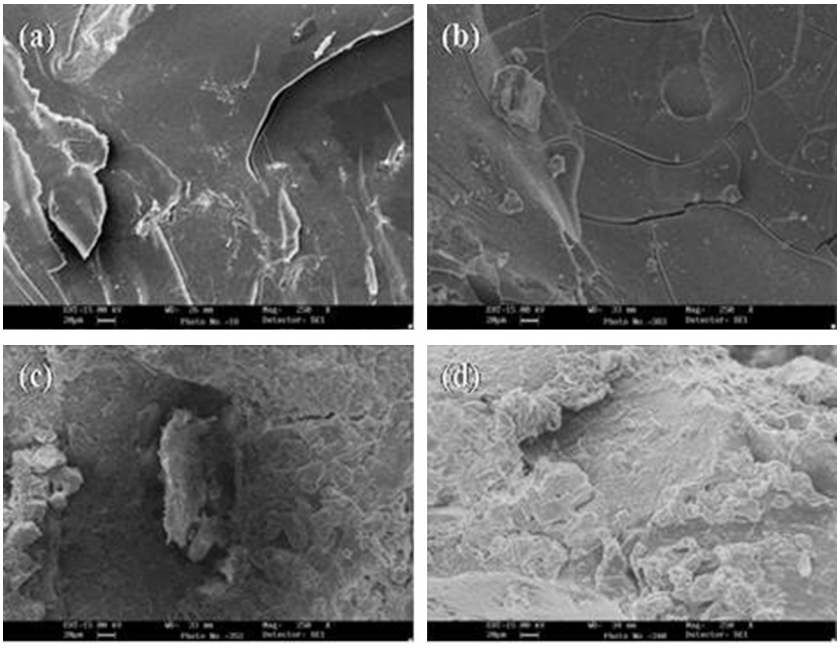



**Fig. 4.** SEMs of (a) Gg-cl-poly(AAm-co-AA); (b) biodegradation stage-I of Gg-cl-poly(AAm-co-AA); (g) biodegradation stage-II of Gg-cl-poly(AAm-co-AA); (h) biodegradation stage-III of Gg-cl-poly(AAm-co-AA).

confirms that the grafted chains of poly(AAm-co-AA) and Gg got biodegraded.

*3.5.1.2. SEM.* The morphological behavior of Gg-cl-poly(AAm-co-AA) before and after degradation was studied by using SEM. Fig. 4a–d shows the SEMs of Gg-cl-poly(AAm-co-AA) and the samples of biodegradation stage-I, stage-II and stage-III, respectively. Before degradation Gg-cl-poly(AAm-co-AA) had very smooth and homogeneous surface (Fig. 4a). Whereas, some cracks and fissures started appearing on the surface of Gg-cl-poly(AAm-co-AA) in the biodegradation stage-I and stage-II. This might be due to the starting of the breaking down of crosslinks between different polymeric chains (Fig. 4b and c). In the third and final stage of biodegradation, the surface became completely heterogeneous and the size and number cracks and fissures increased largely (Fig. 4d). This might be due to the complete breakage of the covalent bonds between different polymeric chains through the chemical and enzymatic degradation by the secreted products of different microorganisms.

## 4. Conclusion

New biodegradable flocculants of Gg with AAm-co-AA have been synthesized successfully and the polymer was found to degrade 89.76% within 60 days. The progress of degradation at each stage was confirmed through FT-IR and SEM analysis. Thermal stability of the polymer was found to increase after grafting and crosslinking. Moreover, the candidate polymer swelled up to 1418% in deionized water. Candidate polymer showed pH, temperature and ionic strength of cations dependent swelling behavior. Moreover, it was successfully utilized for the selective removal of saline from different petroleum fraction-saline emulsions. Gg-cl-poly(AAm-co-AA) was also found to show temperature and pH dependent flocculation behavior. Thus, the preparation of such green hydrogels is an important step from technological point of view and opens the doors of their utilization in many industrial applications like drug delivery and waste water treatment in future.

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