



Microwave assisted synthesis of polyacrylamide grafted starch (St-g-PAM) and its applicability as flocculant for water treatment

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ABSTRACT

Polyacrylamide grafted starch (St-g-PAM) was made by a novel method of synthesis, involving combination of microwave radiation and a chemical free radical initiator (ceric ammonium nitrate) to initiate grafting reaction. This method (microwave assisted synthesis) is quick, highly reliable, reproducible and yields high quality product as compared to the conventional method (which uses a chemical free radical initiator alone to initiate the grafting reaction). The St-g-PAM grades synthesized were characterized by various physicochemical techniques. Further, its application as flocculant for wastewater treatment was investigated.

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1. Introduction

The importance of graft copolymers in the world of polymer science is analogous to the importance of alloying in case of metals. In case of grafted polysaccharides this assumes even greater importance as grafting is perhaps the most effective way of regulating the properties of polysaccharides 'tailor-made' according to our needs.

The main problem in case of graft copolymers is the lack of commercial methods of synthesis. The chief methods of synthesis of grafted polysaccharides involves use of chemical free radical initiator (conventional method), high energy radiations (gamma and X-ray), UV-radiation based method and microwave based methods.

The conventional method of synthesis uses a chemical free radical initiator (e.g. ceric ammonium nitrate or CAN) to generate free radical sites on the backbone polymer, where the monomer of the graft gets added up to form the graft chain [1–5]. This method of synthesis has low reproducibility and is not very suitable for commercial scale synthesis.

A better method of graft copolymer synthesis is by use of high energy radiation (gamma rays or electron beam) as the free radical generator [6–7]. But this method is not suitable for grafted polysaccharide synthesis as the high energy radiation can cause damage to the polysaccharide backbone (radiolysis).

UV rays in presence of suitable photosensitizer can also be used, but low penetration of UV-rays makes it suitable for surface grafting only.

The best method of graft copolymer synthesis is by use of microwave radiation to generate the free radical sites on the backbone polymer. Recently, the microwave based methods of graft copolymer synthesis has been classified into two types [8]:

- (1) Microwave initiated synthesis: uses microwave radiation alone to create free radical sites on the polysaccharide backbone, from where the graft chains grow [4,8–10].
- (2) Microwave assisted synthesis: uses a combination of microwave radiation and chemical free radical initiator to create the free radical sites on the polysaccharide backbone, from where the graft chains grow.

In the study reported here, we have synthesized polyacrylamide grafted starch (St-g-PAM) by 'microwave assisted' method, in presence of ceric ammonium nitrate (CAN) as free radical initiator. Microwave assisted synthesis of grafted starch using CAN as free radical initiator, has never been reported before to the best of our knowledge.

Grafted polysaccharides have diverse applications, cutting across various fields of science and technology. Some important applications are as flocculant for wastewater treatment [4,9], as matrix for controlled drug release [8,10] and rheological applications. In this study, we have investigated the flocculation efficacy of polyacrylamide grafted starch (St-g-PAM) synthesized by microwave assisted process, towards its application in wastewater treatment.

Water is the single most important resource that decides the fate of human being and for that matter any living being. The present ever increasing population and improving standard of liv-

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ing, coupled with depleting water resources have put a strong case on recycling of wastewater. Flocculation is an effective way of treating wastewater as it not only removes the colloidal particles (as floc) but also the heavy metals and other contaminants that gets adsorbed in them. Further, these flocculated colloidal particles include most of the microbes present in the wastewater. Also, removal of colloidal particles makes sterilization of the water easy as the microbes cannot get shelter against the colloidal particles and hence gets full exposure to the sterilizing radiations.

Flocculation is a technique where polymers are involved in a solid–liquid separation by an aggregation process of colloidal particles [11]. Both synthetic and natural polymers have been utilized for flocculation. The advantage of flocculation over coagulation is that the former uses only polymeric materials in minute quantities. These polymeric materials are mostly physiologically inert and are biodegradable. On the other hand, coagulation involves use of inorganic salts (e.g. alums) for charge neutralization of colloidal particles. These inorganic salts are required to be added in higher doses and their very presence in the water can lead to detrimental effects (e.g. aluminium exposure due to use of alum as coagulant, can lead to Alzheimer's disease over long term [12]).

2. Materials and methods:

2.1. Materials

Maize starch and ceric ammonium nitrate were supplied by E. Merck (India) Limited, Mumbai, India. Acrylamide was procured from E. Merck, Germany. Analar grade of acetone and hydroquinone was purchased from S.D. Fine Chemicals, Mumbai, India. All the chemicals were used as received; without further purification.

2.2. Synthesis

2.2.1. Microwave assisted synthesis of polyacrylamide grafted starch (St-g-PAM), using ceric ammonium nitrate (CAN) as free radical initiator

1 gm of starch was dissolved in 40 ml distilled water. Desired amount of acrylamide was dissolved in 10 ml water and was added to the starch solution. They were mixed well and were transferred to the reaction vessel (1000 ml borosil beaker) and catalytic amount of ceric ammonium nitrate (CAN) was added. The reaction vessel was subsequently placed on the turntable of a microwave oven. Now, microwave irradiation at 800 W of power was performed. Periodically, the microwave irradiation was paused just before boiling of the reaction mixture starts (~65 °C) and was cooled by placing the reaction vessel in cold water. This was done to keep the competing reaction of homopolymer formation to the minimum and also to prevent formation of vapours, which may contain acrylamide and hence can be toxic/carcinogenic.

This microwave irradiation – cooling cycle was repeated until a gel like mass was left or up to 3 min of irradiation time (if no gelling took place). Once this microwave irradiation process was complete, the reaction vessel and its contents were finally cooled and kept undisturbed for 24 h, to complete the grafting reactions. Now, the gel like mass left in the reaction vessel was poured into excess of acetone. The resulting precipitate of graft copolymer was collected and was dried in hot air oven. Subsequently, it was pulverized and sieved. The percentage grafting of this microwave assisted synthesized St-g-PAM was evaluated as:

$$\% \text{grafting} = \frac{\text{wt. of graft copolymer} - \text{wt. of polysaccharide}}{\text{wt. of polysaccharide}} \times 100$$

The proposed mechanism of synthesis has been depicted in Scheme 1 and the synthesis details of various grades of the graft copolymer have been shown in Table 1.

2.2.2. Purification of the graft copolymer by solvent extraction method

Any occluded polyacrylamide (PAM) formed by competing homopolymer formation reaction was removed from the grafted polymers synthesized as above, by solvent extraction using a mixture of formamide and acetic acid (1:1 by volume) [13].

2.3. Characterization

2.3.1. Intrinsic viscosity measurement

Viscosity measurements of the polymer solutions were carried out with an Ubbelodhe viscometer (constant: 0.003899) at 25 °C. The viscosities were measured in aqueous solutions. The pH of the solution was neutral. The time of flow for solutions was measured at four different concentrations. From the time of flow of polymer solutions (t) and that of the solvent (t_0 , for distilled water), relative viscosity ($\eta_{rel} = t/t_0$) was obtained. Specific viscosity was calculated from the relation $\eta_{sp} = \eta_{rel} - 1$. Then, the reduced viscosity (η_{sp}/C) and the inherent viscosity ($\ln \eta_{rel}/C$) were calculated, where 'C' is the polymer concentration in g/dL. The intrinsic viscosity was obtained from the point of intersection after extrapolation of two plots, i.e. η_{sp}/C versus C and $\ln \eta_{rel}/C$ versus C, to zero concentration [14]. The intrinsic viscosity of the various grades of the graft copolymers has been given in Table 1.

2.3.2. Elemental analysis

The elemental analysis of starch and that of St-g-PAM 2 (best grade of the grafted starch synthesized) was undertaken with an Elemental Analyzer (Make – M/s Elementar, Germany; Model – Vario EL III). The estimation of five elements, i.e. carbon, hydrogen, nitrogen, oxygen and sulphur were undertaken. The results have been summarized in Table 2.

2.3.3. FTIR spectroscopy

The FTIR spectrums of starch (Fig. 1(a)) and of St-g-PAM 2 (Fig. 1(b)) were recorded in solid state, by KBr pallet method using a FTIR spectrophotometer (Model IR-Prestige 21, Shimadzu Corporation, Japan) between 400 and 4000 cm^{-1} .

2.3.4. Scanning electron microscopy

Surface morphology of starch (Fig. 2(a)) and St-g-PAM 2 (Fig. 2(b)) were analyzed in scanning electron microscopy (SEM) in powdered form (Model: JSM-6390LV, Jeol, Japan).

2.3.5. TGA studies

The thermo gravimetric analysis (TGA) of starch and that of the St-g-PAM 2 were carried out with TGA instrument (Model: DTG-60; Shimadzu, Japan). The study was performed in an inert atmosphere (nitrogen) from 25 °C to 600 °C. The heating rate was uniform in all cases at 5 °C/min. The concerned TGA curves have been shown in Fig. 3(a) and (b).

3. Flocculation studies

Flocculation efficacies of various synthesized grades of St-g-PAM were studied by standard jar test procedure, in 0.25% kaolin suspension.

All flocculation experiments were carried out in jar test apparatus (Make: Simeco, Kolkata, India). The test protocol involved taking a measured quantity (800 ml) of the 0.25% suspension in 1000 ml borosil beaker. Calculated amount of the flocculant (starch or various grades of St-g-PAM) was added in concentrated solution form (except in case of blank, where no flocculant was added) to achieve the desired concentrations (ranging from

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