



# A novel polymeric flocculant based on polyacrylamide grafted inulin: Aqueous microwave assisted synthesis



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## ABSTRACT

Polyacrylamide grafted inulin (In-g-PAM) was synthesized via *aqueous microwave assisted* method (using ceric ammonium nitrate in synergism with microwave in aqueous medium). The intended grafting of the PAM chains on polysaccharide backbone was confirmed through standard physicochemical characterization techniques, namely intrinsic viscosity measurement, Fourier transform infrared (FTIR) spectroscopy, elemental analysis (C, H, N and O), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) studies. Flocculation efficacy of various grades of synthesized grafted product was studied in coal fines suspension, in relation to inulin (parent polysaccharide). This was done utilizing *jar test* and *settling test* procedure, towards possible application as a flocculant for coal washery effluents.

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## 1. Introduction

### 1.1. Inulin – isolation, uses and chemical structure

Inulin is a natural and abundant, renewable polysaccharide that is found in many regularly consumed vegetables, fruits and cereals as a storage carbohydrate (Van Loo, Coussement, De Leenheer, Hoebregs, & Smits, 1995). After starch, they are the most plentiful carbohydrates occurring in plant kingdom. First isolated from the roots of *Inula helenium* (perennial herbs of *Compositae* family), inulin is industrially produced from chicory roots (*Chicorium intybus*) and Jerusalem artichoke (*Helianthus tuberosus*) (Kaur & Gupta, 2002). Dahlia (*Dahlia pinnata*) and yacon (*Smallanthus sonchifolius*) tubers are some of its other important sources.

Inulin is a nondigestible polyfructose having many diverse applications. It is widely used in food, feed, biofuels, water purification and pharmaceutical industries. In food industry, it is used as a sweetener, a fat substitute and as a vehicle to increase the fibre content of the diet (Roberfroid, 2007). It is also used as a live-stock feed and pet food (Verdonk, Shim, Van Leeuwen, & Versteegen, 2005). It can be used for production of ultrahigh fructose syrup, bioethanol as well as chemicals like citric acid, 2,3-butanediol etc. (Chi et al., 2011). Inulin derivatives are used as green antiscalants in

industrial water treatment processes (Mavredaki, Stathouloupoulou, Neofotistou, & Demadis, 2007). It has been classified as a bifidogenic prebiotic (Veereman, 2007) and owing to their anticarcinogenic properties (Korbelik & Cooper, 2007), inulin derivatives are being used as colonic drug delivery systems (Pitarresi et al., 2008).

From a chemical point of view, inulin is a polydisperse fructan. Its structural motif consists mainly, if not exclusively of  $\beta$  (2 → 1) fructosyl fructose units ( $F_m$ ) with normally, but not necessarily, one glucopyranose unit at the reducing end ( $GF_n$ ) (De Bruyn, Alvarez, Sandra, & De Leenheer, 1992). Inulin containing glucopyranose unit is not a reducing sugar. The fructose units in the polysaccharide are all present in the furanose form, except when the reducing end consists of fructose (Rogge & Stevens, 2004). When this is the case, terminal fructose is present in the pyranose form giving to inulin reducing properties. In general, reducing properties of inulin are a rarity since chain termination by glucopyranose is dominant.

### 1.2. Graft copolymerization: processes, mechanism and role of microwave

A graft copolymer consists of a long sequence of one monomer, referred to as the backbone polymer (main chain) with one or more branches (grafts) of a different monomer (Gowariker, Vishwanathan, & Sreedhar, 1986). Synthetic protocols for graft polymerization can be classified into three main groups, namely: a) free radical polymerization b) ionic and ring opening polymerization and c) living radical polymerization. The above polymerization techniques broadly involve following mechanistic approaches: a) 'grafting-to' b) 'grafting-from' and c) 'grafting-through', the

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polysaccharide (O dian, 2004). The 'grafting-from' approach mentioned here involves the use of a natural polymer with pendant functional group that can be activated to initiate the tethering of an incoming monomer. This is one of the most commonly used approaches and gives products with high graft density owing to easy accessibility of the reactive groups (Roy, Semsarilar, Guthrie, & Perrier, 2009).

In case of free radical polymerization, grafting process starts with generation of radical sites on the backbone polymer (polysaccharide in this case) using an external agent. Once the free radical sites are generated, the monomer (i.e., vinyl or acrylic substrate) can get anchored to the backbone polymer in the chain propagation step; resulting in formation of grafted products. All the various modes of graft copolymer synthesis, whether utilizing high energy UV radiation or Microwave, primarily differ in the ways of generation of free radicals on the backbone polymer.

Use of microwave radiations is one of the most contemporary techniques in graft copolymer synthesis. Their utility stems from the fact that they cause selective and targeted excitation of only the polar bonds, resulting in their cleavage and consequent generation of free radical sites (Sen, Kumar, Ghosh, & Pal, 2009). The 'C–C' backbone of the preformed polymer being relatively non polar, remains unaffected by the microwave radiation. Thus, the structural integrity of the backbone remains intact, leading to a superior product (Rani, Mishra, & Sen, 2013). Microwave based graft copolymer synthesis is further classified into two types: Microwave initiated synthesis (using microwave radiation alone to initiate grafting) and microwave assisted synthesis (using a synergism of microwave radiation and chemical free radical initiator to initiate grafting) (Ghosh, Sen, Jha, & Pal, 2010).

### 1.3. Significance of aqueous medium, coal fines flocculation and PAM chain grafting

Taking into account, environmental and safety considerations, attempts to replace toxic organic solvents by safer and more environment friendly medium present an arduous task. In this context, water appears to be a better option compared to organic solvents because of its abundance, non-toxic, non corrosive and non flammable nature. In addition, water can be contained because of its relatively higher vapour pressure as compared to other solvents, making scale up easier. Although *microwave assisted* reactions in conventional solvents have developed rapidly, the centre of attention has now shifted to greener and sustainable alternatives such as water (Dallinger & Kappe, 2007; Polshettiwar & Varma, 2008).

Coal consumption, has been for long, an important indicator of a nation's economic growth. Especially for the developing world, with its high energy requirements and abundant supply of coal, it is hard to ignore their economy's coal reliance. In this context, washing and cleaning coking coals before their varied industrial use has gained currency. The trouble though is the very process of cleaning produces effluents consisting of coal fines suspension. These coal washery effluents could pollute large stretch of water bodies but if recovered can serve as a precious fuel. Thus, we need to formulate a scheme which could not only take into account the ecological concerns but also the economic viability of the process. Flocculation aided by biodegradable polymeric flocculants seems to be a highly effective strategy in this regard (Pal, Sen, Karmakar, Mal, & Singh, 2008; Tripathy, Pandey, Karmakar, Bhagat, & Singh, 1999).

Tethering synthetic polymers onto natural polymers results in formation of adducts having controlled biodegradability and longer shelf life. PAM family of polymers and copolymers is a highly useful and multifaceted group in this regard, owing to their properties (Caulfield, Qiao, & Solomon, 2002). They have versatile tailorability and the amide groups can be tuned according to the

requirement (Sen, Ghosh, Jha, & Pal, 2011; Yamamoto & Sefton, 1996). Grafting, synthetically stitches flexible PAM branches on the rigid polysaccharide backbone, resulting in better approachability to the colloidal particles and thus better flocculation efficacy (Nayak & Singh, 2001). In addition, low toxicity and low operational investments required for these water soluble, high molecular weight compounds, makes the use of PAM flocculants highly desirable.

### 1.4. Plan of investigation

The study described in this paper (Scheme 1) involves the synthesis of graft chains of polyacrylamide (PAM) onto the backbone of inulin (In), resulting in formation of polyacrylamide grafted inulin (In-g-PAM). The synthesis has been carried out by *aqueous microwave assisted method*, which involves a synergism of microwave radiations and ceric ammonium nitrate (CAN) to initiate the grafting reaction in aqueous medium. The flocculation efficacy of the grafted product has been studied in coal fines effluent towards its application in coal washery effluent treatment.

## 2. Experimental

### 2.1. Materials

#### 2.1.1. Materials for synthesis

Inulin was procured from SRL, Mumbai, India and acrylamide was obtained from E. Merck, Germany. Ceric ammonium nitrate was supplied by Loba Chemie, Mumbai, India. Acetone was purchased from Rankem, New Delhi, India. All the chemicals were used as received, without further purification.

#### 2.1.2. Materials for flocculation

The non-coking coal sample utilized in the present study was collected from Piparwar Coal mines, Central Coalfields Limited, Jharkhand, India. Proximate analysis results of the coal sample are given in Supplementary Table 1. The coal sample was pulverized to –200 mesh ASTM (i.e., size <75 μm) for conducting the experiments.

### 2.2. Synthesis

#### 2.2.1. Aqueous microwave assisted synthesis of polyacrylamide grafted inulin (In-g-PAM)

1 g of inulin was dissolved in 40 mL distilled water and to it was added desired amount of acrylamide. The above solution was mixed well and transferred to the reaction vessel (250 mL borosil beaker) followed by addition of catalytic amount of free radical initiator, ceric ammonium nitrate. The reaction vessel was placed on the turntable of a microwave oven and microwave irradiation at a power of 800 W was performed. Periodically, the microwave irradiation was paused just as the reaction mixture starts boiling (~65 °C) and was cooled by placing the reaction vessel in cold water. This was done to keep any probability of competing homopolymer formation reaction to the minimum.

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). The reaction vessel and its contents were then cooled and kept undisturbed to complete the grafting reaction. Later, 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 a hot air oven. Subsequently, it was pulverized, sieved and purified. The percentage grafting of this microwave assisted synthesized In-g-PAM was evaluated as:

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

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