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Synthesis and characterization of polymethylmethacrylate grafted barley for treatment of industrial and municipal wastewater

Kartick Prasad Dey, Sumit Mishra*, Gautam Sen

Department of Chemistry, Birla Institute of Technology-Mesra, Ranchi 835215, Jharkhand, India

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A B S T R A C T

In the present investigation, we have synthesized polymethylmethacrylate grafted barley (BAR-g-PMMA) using ceric ammonium nitrate as an initiator and methyl methacrylate as monomer in the presence of nitrogen atmosphere. The different grades of polymethylmethacrylate grafted barley were prepared by varying the concentration of initiator and monomer till the best grade was optimized. The synthesized grades have been confirmed by different analytical techniques like FTIR spectra, elemental analysis, TGA analysis, XRD analysis, intrinsic viscosity measurement, SEM morphology and number average molecular weight determination. The flocculation efficiency of the developed materials has been tested in coal fine, iron ore and kaolin suspensions. The best grade showed 86, 75 and 82% flocculation efficiency in coal fine, iron ore and kaolin suspension respectively and this was found to be 1.21, 1.25 and 1.24 times better than commercial flocculant Polyacrylamide. The settling rate was also determined during flocculation study. This material was further applied for treatment of municipal waste water. The acute oral toxicity of this material has been studied following Organization of Economic Co-operation and Development (OECD) guidelines showing its non toxic nature. Overall, on the basis of the above results, the developed non toxic graft copolymers can be safely used for treatment of the municipal as well as industrial waste water.

1. Introduction

Fresh water is essential for human survival, agricultural and industrial activities. The shortage of fresh water is one of the major challenges worldwide [1,2]. This problem is aggravating day by day and creating endless demand of clean water due to increase in population, higher living standards, urbanisation etc. Around 0.35 billion people from 25 different countries (particularly from Middle east and Africa) are suffering from water shortage and this may shoot upto 3.9 billion in 52 countries by 2025 [3,4].

The major part of waste water comes from domestic and Industrial sources [5]. This type of waste water is contaminated by the toxic metals, micro and macroparticles, bacteria, other pathogens, toxic dyes, different types of inorganic and organic particles [6,7]. This is directly disposed off in rivers, seas or percolates ground water table which leads them to our food cycle. It enters human physiology which serves as an ideal host for various types of micro organisms [8,9].

Presently, numerous efforts are being taken towards sustainable water resource management. Flocculation is widely used for the treatment of different types of waste water such as palm oil mill effluent, textile waste water, pulp mill waste water, oily waste water, sanitary landfill leachates and many more [10,11]. Flocculation involves the addition of chemicals along with agitation which aids sedimentation or adsorption leading to removal of heavy metals, micro organism or other solids leading. The flocculation process destabilizes solid particles for the formation of larger aggregates. It also aggregates heavy metals and organic materials on the surface of the flocculants by the weak electrostatic interactions [12,13].

In waste water, the characteristics of the solid particles are influenced by the electro kinetic charges. The colloidal impurities in waste water contain negative charges developed due to the presence of polar groups such as carboxylic and amine groups [14]. The size of the colloidal particles range between 0.01–1 μm and the attractive forces among them are less compared to repulsive forces due to electrical charges [15]. As a result, the particles are suspended in water. In order to settle these suspended colloidal particles, the first step is to destabilize them followed by formation of larger aggregates. So, the weight of the aggregated particles increases and it settles down as a floc due to gravity [16].

Nowadays, polysaccharide based flocculants have received much attention for waste water treatment processes. The demand of these materials is increasing day by day due to several advantages over other

* Corresponding author.
E-mail address: sumitmishra1@gmail.com (S. Mishra).

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counterparts such as eco friendly, easy availability, low cost, biocompatibility and easy to modify for several applications [17,18]. Besides their several unique advantages, they have some disadvantages also like poor physical and mechanical properties which restrict their application. These restrictions can be overcome by their chemical modification with different types of acrylic and vinyl monomers [19–25]. Various techniques are used for the modification of these polysaccharides. Recently, the graft copolymerization has attained a unique status for modification of polysaccharides. Grafting can be achieved by conventional redox method, microwave initiated method, microwave assisted method, γ-ray irradiation, electron beams and photochemical methods [26–29]. Among these methods, the conventional redox method is the most widely accepted technique for the modification of the polysaccharides to achieve the desirable properties as per their potential use.

Among the various types of polysaccharides, barley (*Hordeum vulgare L)* plays an important role since ancient times. It is an agricultural crop well known throughout the world. The main chemical component of barley is polysaccharide (i.e. 90–95%) and rest are protein and fats. Starch and dietary fibres are the main components of the barley polysaccharide [30]. Starch is a carbohydrate molecule made up of large number of glucose units joined through glycosidic bonds. Starch consists of about 25–30% amylase and rest amylopectin. Amylose is a linear carbohydrate made up by D-Glucose unit and bonded through α(1 → 4) glycosidic bonds. Amylopectin is a branched carbohydrate of glucose made up by glucose units bonded in a linear way by α(1 → 4) glycosidic bonds and branching with every 24–30 repeating glucose units. Dietary fibres are made by the D-Glucose monomer linked by β-glycoside bond through 1, 3 & 1, 4 carbon atom of repeating glucose units respectively. Till now, barley is used for production of beer and other liquors like brandy, whisky and some medical purposes. The modification of barley is needed to suit various applications [31].

Among the various types of natural polysaccharides, the food grade polysaccharides play an important role as a flocculant due to their non toxic nature, economic viability and widespread cultivation [32,33]. Barley satisfies all these criteria in terms of abundant cultivation, low price and it is considered as safe and reliable material since ages. The municipal waste water treatment by adding chemicals is directly related with human metabolic system. So, we need safe material and flocculants must be non toxic in nature. The food vs chemical crisis does not arise here because it is used in a small quantity given the fact that it is the 4th most abundant crop worldwide. The polymethylmethacrylate polymer is biocompatible in nature and is already used in water treatment as well as in biomedical field successfully [34,35]. Bar-g-PMMA has not been used for water treatment applications till now, so we have explored this material and found it to be an efficient flocculant. Hence, this project is novel and not reported so far anywhere.

In this research article, we report the successful synthesis of novel BAR-g-PMMA graft copolymer by conventional redox grafting process. Ceric ammonium nitrate is used as radical initiator for polymerization reaction. The synthesis has been confirmed by the various analytical techniques. The flocculation efficiency of the developed materials is performed in various synthetic waste waters and assessed for its application in water treatment. The acute oral toxicity of the synthesized materials has been studied. On the basis of our experimental results, the BAR-g-PMMA and its derivatives can be safely used for municipal and industrial waste water effluents.

2. Experimental

2.1. Materials

Barley was purchased from Reckitt Benckiser, Ltd. New Delhi, India. Acrylamide and Acetone was supplied by Rankem (AR grade), India and Ceric ammonium nitrate was supplied from E.Merck, Mumbai, India. Methylmethacrylate and kaolin was Acros Organics, India. Polyacrylamide was supplied by HIMEDIA, Mumbai, India. Coal fine and Iron ore were collected from Jharkhand state, India. All of the chemicals were used without further purification.

2.2. Synthesis of BAR-g-PMMA by radical polymerization

The BAR-g-PMMA was synthesized following the radical polymerization pathway. In this procedure, 1gm of barley was taken in 250 ml round bottom flask and mixed with 40 ml of distilled water at 40–45 °C under 30 min of stirring. Then it was kept at room temperature under stirring till it cooled down. Methylmethacrylate was added in this reaction mixture in varying amounts and kept under stirring condition for 15 min to make a homogeneous mixture. Afterwards, nitrogen gas was purged in the reaction mixture followed by test amount of ceric ammonium nitrate in 0.1(N) HNO_3 along with nitrogen purging. Then, the reaction mixture was left undisturbed for 24 h at room temperature [36,37]. The highly viscous reaction mixture was obtained in the reaction vessel after 24 h. A saturated solution of hydroquinone was added in the gel like mass for the completion of graft copolymerization reaction. It was poured in excess acetone. A white coloured gel like precipitate was obtained in the reaction vessel and it was kept in excess acetone. After that, gel like mass was poured in distilled water and kept for 1 h for washing the unreacted part. Again, the gel like mass was poured in acetone. Then, the precipitate was collected and dried in hot air oven till a constant weight was obtained.

The concentration of methylmethacrylate as monomer and ceric ammonium nitrate as initiator were taken w. r. to fixed barley concentration i.e. 1 g. The optimized concentration of monomer and initiator were evaluated w. r. to percentage grafting, intrinsic viscosity and number average molecular weight for the synthesis of BAR-g-PMMA. The synthesis details for all parameters of the graft copolymer have been tabulated in Table 1.

2.3. Purification of synthesized BAR-g-PMMA by solvent extraction

The synthesized materials were kept in excess acetone for 72 h for removal of any homopolymer (polymethylmethacrylate). They were collected from excess acetone and again dried in hot air oven till a constant weight was obtained [38]. The percentage grafting was calculated on the basis of following formula.

$$P_g = \frac{W_g - W}{W} \times 100 \quad \text{(i)}$$

Here, W is weight of barley, W_g is the weight of grafted product and P_g is the percentage of grafting. All the synthesis parameters are summarised in Table 1.

Table 1
Synthesis details of BAR-g-PMMA by *"Conventional method"*.

Polymer Grade	Wt. Of Barley (gm.)	Wt. Of methyl methyacrylate (gm.)	Wt. Of CAN (gm.)	% of grafting (% G)	Intrinsic viscosity (dl/g)	Number average molecular weight (k Da)
G-1	1	10	0.1	8.76	1.83	1234
G-2	1	10	0.2	47.42	3.05	2456
G-3	1	10	0.3	66.89	3.78	2987
G-4	1	10	0.4	114.74	5.64	3456
G-5	**1**	**10**	**0.5**	**166.89**	**10.34**	**7435**
G-6	1	10	0.6	89.06	8.76	5436
G-7	1	12.5	0.5	72.38	7.08	4325
G-8	1	15	0.5	68.56	6.12	3987
Barley	0	0	0.0	0.0	1.83	176.6