ASI

Carbon – Science and Technology

ISSN 0974 – 0546

http://www.applied-science-innovations.com

RESEARCH ARTICLE Received:10/03/2016, Accepted: 23/06/2016

Algal biomass harvesting by graft copolymer of polyacrylamide on guar gum (GG-g-PAM): a sustainable method for alternative source of energy

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Abstract: Microalgal cells has been utilized as a rich source of food, feed and fuel. The process of concentrating algal cells from water suspension is called harvesting. This article deals with the algal biomass harvesting by flocculation process using acrylamide grafted guar gum. Acrylamide has been successfully grafted onto the backbone of guar gum by microwave initiated method in which microwave radiation alone (without chemical free radical initiator) is used to initiate the grafting reaction. Simultaneously with the synthesis of graft copolymer, water removal capability of various grades of GG-g-PAM have also been studied as a flocculant for algal biomass harvesting through standard jar test procedure for collection of algal biomass. The collected biomass can be hand carried. The collected biomass has been characterized in terms of crude fat content and elemental composition. Calorific value of this collected biomass has also been theoretically calculated.

Keywords: Graft copolymer, flocculation, algal biomass harvesting, biofuel

1 Introduction: Because of the tremendous and ever increasing pressure of dwindling non- renewable energy assets, increasing planet's ecological concern and sustainable economy, we need to switch to some other sustainable alternative sources of energies like solar energy, tidal, wind, geothermal, bioenergy, hydrogen fuel cells, nuclear fusion etc. In fact we are moving there, but some of them are still in the experimental stages. Algae, earth's oldest organism are emerging to be potential, renewable and green energy source to reduce or eliminate existing sources in terms of availability, affordability and earth- friendly inclination. Algae contain energy in the form of carbohydrates and oils. After extraction of oil, the remaining residue can be used as fuel in power generation plants, industrial furnaces and boilers.

Microalgae has been harvested by various water removing methods which include sedimentation, centrifugation, filtration, use of biological and chemical methods, electrical separation methods etc.**[1, 2]**. All these methods have one or more of the disadvantages like operational feasibility, economic issues, skilled labor requirement etc. Since last few decades, it has been observed that polymeric materials havebeen successfully employed in flocculation based applications ranging from mineral ore beneficiation to wastewater treatment **[3, 4]**.Recent studies have been shown that polyacrylamide based graft copolymer of polysaccharide have excellent flocculation performance than parent polysaccharide and synthetic polymeric flocculant, since graft copolymer has dangling, flexible chains of polyacrylamide onto the rigid polysaccharide backbone which in turn make the approachability of contaminant particles (algal cells) to the graft copolymer easy, causing them to clump together and settle down at the bottom of vessel as floc **[5]** and remaining water may be used for various other purposes.The collected algal biomass can be converted into various types of renewable fuels like biodiesel, aviation fuel, green gasoline, alcohol fuels, methane biogas, ethanol and butanol **[6]**.

This paper describes a contemporary method of synthesis of acrylamide grafted guar gum (GG-g-PAM)by microwave initiated method as described in an earlier study [7].Further, flocculation studies of synthesized grades of the novel graft copolymer have been performed in algal biomass suspension by standard jar test procedure. The high flocculation efficacy of GG-g-PAM makes it highly useful in the field of algal harvesting as it results in speculative (spectroscopic) along with actual (on hand) collection of biomass.The collected biomass has been characterized in terms of crude fat content and elemental composition. Calorific value of this collected biomass has also been measured theoretically by Dulong Formula.

2. Materials and methods:

2.1. Materials: Algal suspension was collected from natural water reservoir nearby the BIT, mesra campus. It was a mixed culture of algal cells.

2.2 Synthesis of graft copolymer of Guar gum (GG-g-PAM) by microwave initiated method:

As per the earlier study, a series of all three grade of GG- g– PAM [7] was synthesized by the microwave initiated method as follows. 1 g of guar gum was dissolved in 40 mL distilled water. 10 g of acrylamide was dissolved in 10 mL water and was added to the above solution. They were mixed well. The reaction vessel was subsequently placed on the turntable of a microwave oven. Then, microwave irradiation at 900W of power was performed. Periodically, the microwave irradiation was paused just before boiling of the reaction mixture started and was cooled by placing the reaction vessel in cold water. This microwave *irradiation – cooling* cycle was repeated up to desired time. Once this microwave irradiation process was complete, the reaction vessel and its contents were finally cooled and kept undisturbed for 24 hrs, 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. All synthesized grades were purified by solvent extraction method as described earlier [7]. The percentage grafting of the all grades of GG- g- PAM was calculated from the equation:

$$\% \text{ Grafting} = \frac{\text{Wt. of graft copolymer - Wt. of Polysaccharide}}{\text{Wt. of Polysaccharide}} \times 100 \qquad (1)$$

The synthesis details of various grades of the graft copolymer have been shown in Table (1). Characterization of synthesized best grade of GG-g-PAM has been studied earlier as reported in the above mentioned paper.

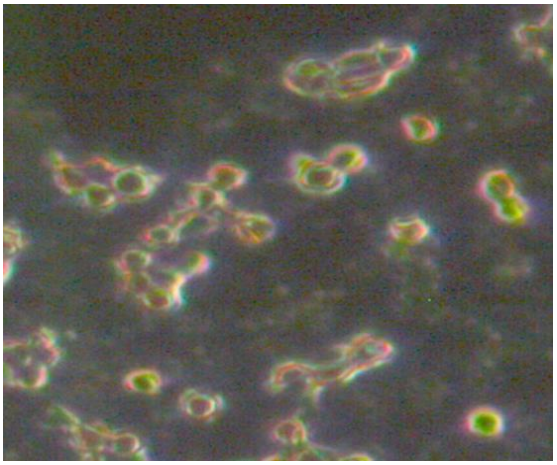
2.3 Characterization of algal biomass

2.3.1 Microscopic analysis: The microscopic analysis of collected algal biomass was studied by optical microscope (Leica DFC 320). These are shown in Figure (1a and b).

2.3.2 Proximate analysis: It includes the analysis of moisture content, volatile combustible matter (VCM), total ash and percentage of fixed carbon content.Moisture was determined by gravimetric method by measuring the loss in weight after heating the sample at 100 ^{0}C for about 1 hr. in a hot air oven till the weight of sample becomes constant.

Table (1): synthesis details of GG-g-PAM.

Grade	Wt. of Guar Gum (g)	Wt. of Acryl-amide (g)	Time (min)	% Grafting
GG-g-PAM 1	1	5	2	31
GG-g-PAM 2	1	5	3	59
GG-g-PAM 3	1	5	4	24


(a)

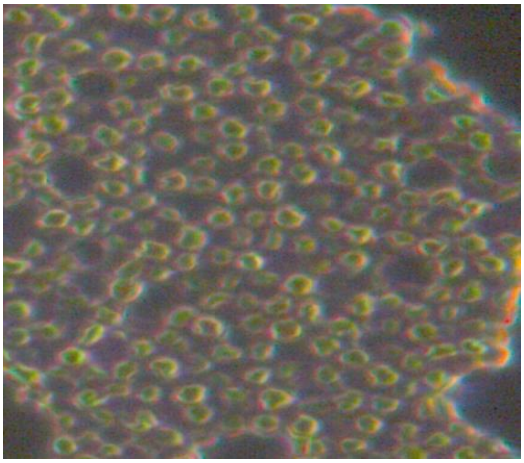

(b)

Figure (1): (a) microscopic picture of algal cells before flocculation, and
(b) microscopic picture of algal cells after flocculation.

Volatile combustible matter (VCM) was also determined gravimetrically by placing the known quantity of dry sample (after removal of moisture content) in muffle furnace at 950 ^{o}C temperature for seven min. The loss in weight represents VCM of biomass. For determination of total ash content, a known quantity of sample is ignited in muffle furnace at 700- 750 ^{o}C temperature for about 30 min till constant weight was obtained. The loss in weight shows total ash content. Fixed Carbon is determined directly by deducting the sum total of moisture, ash and volatile combustible matter from 100.

% of Fixed Carbon= 100- % of (Moisture + VCM + Total ash) (2)

The results of proximate analysis have been reported inTable (2).

2.3.3.Ultimate analysis: The elemental composition of algal biomass was undertaken with an Elemental Analyzer (Make – M/s Elementar, Germany; Model – Vario EL III). The estimation of carbon, hydrogen, nitrogen, and oxygen were undertaken. The results have been given in Table (3).

2.3.4 Determination of calorific value: The amount of heat evolved by complete combustion of fuel is known as calorific value. Calorific value of collected algal biomass (biofuel) was calculated theoretically from elemental composition using *DULONG FORMULA* which is given below.

Calorific value = 1/100 [8080 C + 34500 {H- O/8)} + 2240 S] Kcal/ Kg (3)

where C, H, O and S represent the % of carbon, hydrogen, oxygen and sulphur respectively.

2.3.5 Determination of crude fat by solvent extraction method: Crude fat represents phospholipids, sterols, fat soluble pigments, fat soluble vitamins etc. along with true fat (triglycerides), is extracted by soxhlet extraction method using n-hexane as a solvent for about 12 hrs. The flow chart for method of extraction of crude fat is illustrated in Figure (2).

Table (2): Proximate analysis of algal biomass.

Moisture (%)	VCM (%)	Total ash (%)	Fixed Carbon (%)
10.1	54.5	12.4	23

Table (3): Ultimate analysis of algal biomass.

Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulphur (%)	Oxygen (%)
34.07	8.655	6.314	0.765	50.196

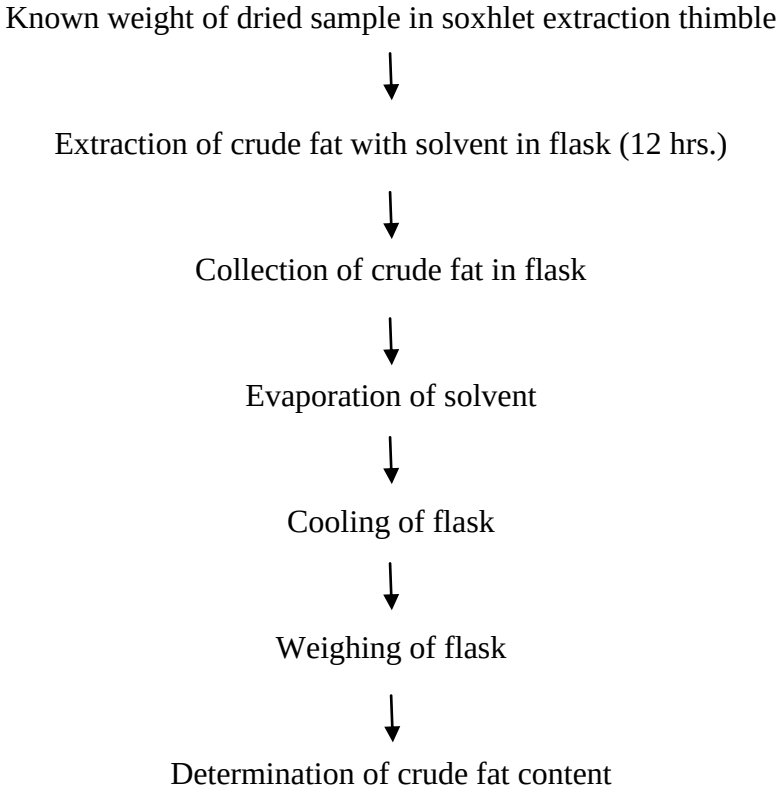


Figure (2): extraction of crude fat.

2.4 Study of algal flocculation efficacy of GG-g-PAM

Flocculation efficacy of all synthesized grades of GG-g- PAM was studied in algal suspension through standard jar test procedure. Calculated amounts of flocculants (various grades of GG-g-PAM) were added to 5 identical beakers containing 200 mL of algal suspension (Figure 3a).The contents of these beakers were stirred identically in a jar test apparatus (Make: Simeco, Kolkata, India) at 300 rpm for 30 sec, 160 rpm for 2 min, followed by 60 rpm for another 10 min. After proper settling,the supernatant liquid was collected from each beaker and optical density (OD) was measured by calibrated UV- Visible spectrophotometer (Elico SL 159) at wavelength 750 nm to plot flocculation graph (Figure 3b). The percentage recovery was evaluated by the equation mentioned earlier **[8, 9]**.

$$\% \text{ Recovery} = \frac{OD_{750}(t_0) - OD_{750}(t)}{OD_{750}(t_0)} \times 100 \qquad (4)$$

where $t_0$is the initial reading (at 0 hr.) and t is the final reading (at time t). Further, the algal suspension in each beaker with optimized dose of flocculent was kept undisturbed for about 3 hrs. The algal biomass settled at bottom was collected by decantation process. It was then dried in hot air oven at about

40 ˚C. Simultaneously, the biomass from control algal suspension was also collected.The percentage recovery by gravimetric method was measured by the equation mentioned below.

$$\text{\% Recovery (Gravimatric method)} = \frac{\text{Wt. of algae recovered by flocculant}}{\text{Wt. of algae in control}} \times 100 \quad (5)$$

The flocculation efficacy thus studied for guar gum and various grades of GG-g-PAM have been graphically illustrated in Figure (3b).

3. Results and discussion:

3.1 Synthesis of graft copolymer of Guar gum (GG-g-PAM) by microwave initiated method: All grade of GG -g-PAM has been synthesized by microwave initiated method as described earlier [7]. The synthesis details have been tabulated in Table (1). The C- H bond breaks preferentially (due to its greater polarity than C- C band) in the presence of microwave irradiation to form free radical site on the backbone of guar gum, from where the graft chains of monomer (acrylamide) grow. The detailed mechanism of synthesis has been discussed earlier [7].

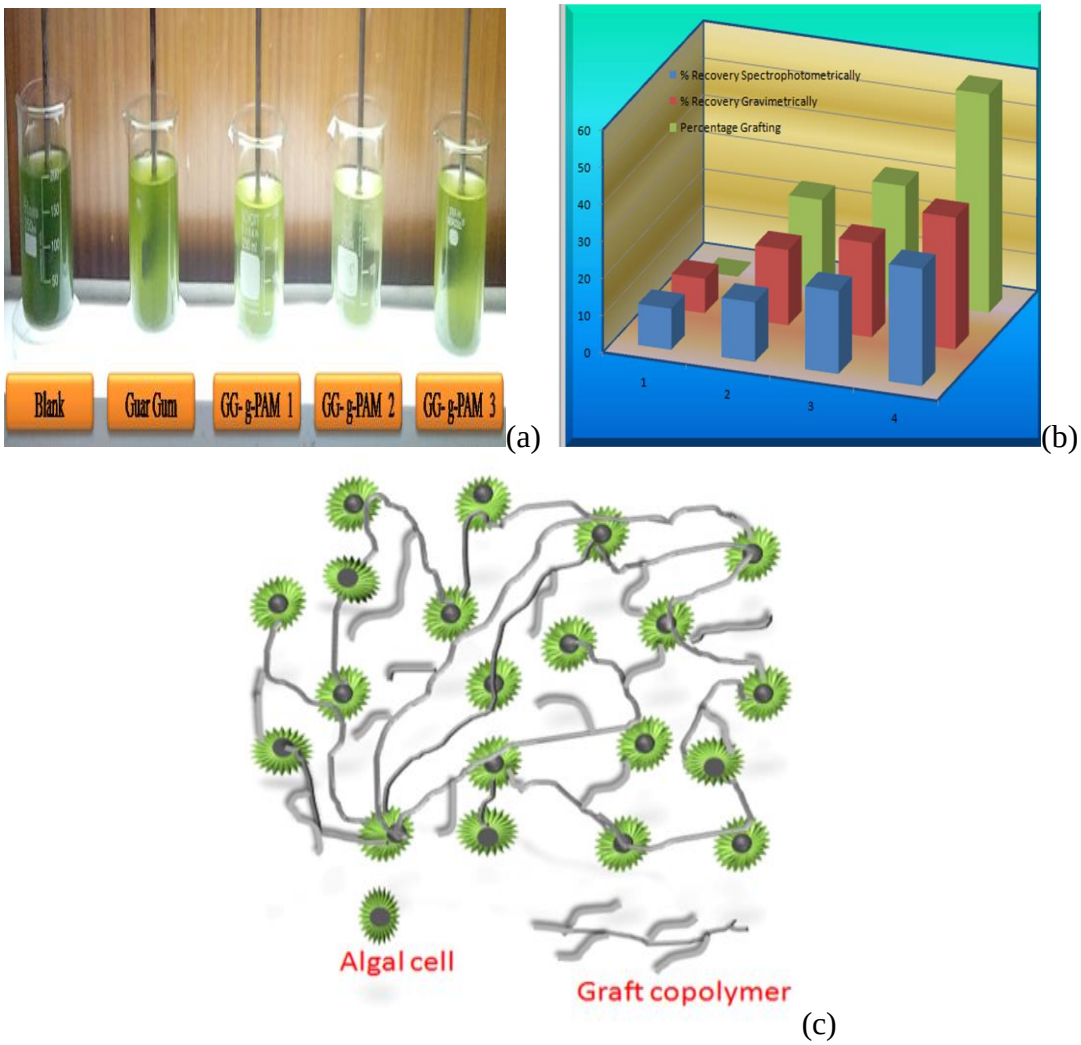


Figure (3): (a) flocculation efficacy of various grades GG-g-PAM in jar test apparatus, (b) flocculation characteristics of Guar Gum and synthesized grades of GG-g-PAM and (c) Mechanistic rationale of algal flocculation.

3.2 Characterization of algal biomass:

3.2.1Microscopic analysis of microalgae: Microscopic pictures of algal cells before flocculation (Figure 1a) shows that different algal cells are uniformly distributed throughout the suspension and algal cells after flocculation (floc) indicate that (Figure 1b) the vitality of algal cells was maintained after flocculation. The cells were alive, flawless and unbroken but clump together in a massive mass. These pictures confirm that algal biomass was not destroyed by flocculation process using GG-g-PAM as a flocculant.

3.2.2 Proximate analysis: The percentage of moisture, volatile combustible matter, total ash and fixed carbon is given in Table (2). The Fixed carbon content of algal biomass is significantly high to be used as fuel.

3.2.3 Ultimate analysis: The percentage composition of element is given in Table (3), which shows that collected biomass is rich in carbon content thus it may be used as biofuel.

3.2.4 Determination of calorific value: The theoretically calculated calorific value of algal biomass by ***DULONG FORMULA*** has been found 3591.26 Kcal/ Kg. It means that collected algal biomass has high calorific value to compete other fuels.

3.2.5 Determination of crude fat content: The percentage of crude fat extracted from algal biomass has been found 32.0% indicating that biomass contain good amount of crude fatwhich is sufficient to be converted into biodiesel/ biofuel.

3.3 Study of algal flocculation efficacy of GG-g-PAM: The long, dangling chains of polyacrylamide get attached onto the straight, rigid backbone of guar gum, form comb like structure. This modified structure enhances the hydrodynamic volume and thus radius of gyration of graft copolymer, this in turn forms bridges between algal cells due to the increase in their approachability **[5]** and every algal cell may connect two or more such type of links.The algal cells get entrapped in this modified structure. In other words, polymeric chains get adsorbed onto the surface of one or more algal cells. In this way, the algal cells draw closer to each other and accumulate in the form of floc which settles down due to the action of gravity.

Among the various grade of GG- g-PAM the optimized grade (GG-g-PAM 2) showed highest flocculation efficacyi.e. most clear supernatant liquid. It can be clearly seen in Fig. 3a. This is due to highest percentage of grafting i. e. highest hydrodynamic volume. The parent polysaccharide (guar gum) showed least flocculation efficacy among various synthesized grades of graft copolymer, due to being of least hydrodynamic volume because it does not have comb like structure of grafted chains.This act of flocculation process exquisitely corroboratesthe bridging mechanism concerned subsequently with the phenomenon **[10, 11]**.

4. Conclusions: An adequate, productive and valuable method for algal biomass harvesting by flocculation induced by graft copolymer of GG-g-PAM was developed. The collected biomass can be used for the production of biofuel/ biodiesel etc. Thus, this technique is capable of lowering the scarcity of fuel demand to a great extent and opens the door for large scale production of algal biomass.

Acknowledgment: Authors acknowledge for the financial support from Department of Science and Technology, New Delhi, India, in the form of research grant (Sanction order No. SR/WOS-A/ET-13/2014) to carry out the reported research. The authors also acknowledge the support of Central Instrumentation Facility (CIF) – BIT Mesra.

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