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Design and development of polyamine polymer for harvesting microalgae for biofuels production ☆

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ABSTRACT

Research findings of the past few decades on the cultivation of microalgae for biodiesel production from laboratory to pilot scale microalgal cultivation have translated into empirical hope of developing an eco-friendly biofuel from algae. As far as economic sustainability is concerned, harvesting of microalgae is one of the most energy extensive processes and thus a major challenge, being faced by this industry. In our study, we designed and developed a quaternary ammonium salt based cationic polymer and evaluated its effectiveness for freshwater microalgae harvesting. An epichlorohydrin-n,n-diisopropylamine-dimethylamine polymer with high viscosity (1040 cps) was synthesized. The flocculation performance of this polyamine polymer was evaluated in terms of biomass recovery efficiency of microalgae (*Scenedesmus* sp.), its effect on lipid yield and composition. The results revealed that due to high molecular weight, the biomass recovery efficiency of the polymer was achieved >90% at a very small dose of 8 mg/L whereas similar biomass recovery efficiency of chitosan and alum were achieved at 80 and 250 mg/L respectively. The presence of functional quaternary amine and hydroxyl groups played an important role in electric charge neutralization of microalgal cells, hence the improved microalgal flocculation performance in comparison to the natural flocculants but not affecting the lipid yield and its composition. The approximate cost of harvesting 1 kg of *Scenedesmus* biomass is approximately 0.5 USD for the polyamine polymer whereas 50 USD for chitosan. Therefore, polymer based harvesting of microalgae for low valued products such as biodiesel, polyamine based polymers would be preferred over the natural polymer.

1. Introduction

Rapid depletion of conventional energy resources has led to a global hunt for renewable sources of fuels, as presently almost 80% of this energy is derived from fossil fuel sources [1]. Economic viability; commercial feasibility and environmental sustainability are three major aspects which are of prime concern for the development of any carbon-neutral biofuels. Microalgae are considered to be self-sustained cell factories which harness and store energy from sunlight that can be used for various purposes from food to fuel [2–4]. They have high productivity whilst utilising limited resources, and have almost 20 times faster growth rates in comparison to oil based crops which contains less than 5% oil of the total biomass basis, thus algae seems to be a potential contender for biofuel production [5,6]. Microalgal species has been reported to contain 20–40% cellular lipids, which could be up to 80% in some of the species under specific growth conditions [7]. The production of biodiesel from microalgae being seen as a panacea for rapidly depleting conventional energy resources [8,9]. It has been established that biodiesel produced from algal lipids, are similar to conventional biodiesel hence can be directly used with little or no modification [10].

Microalgal cells are very small (3–25 μm), negatively charged cells, which remain in suspension form in the culture media as their negative charge prevents aggregation [11]. Microalgal cell walls possess negative charges which originate predominantly due to the presence of carboxylic (–COOH) and amine ($-NH_2$) groups [12]. Therefore, harvesting of such tiny cells by conventional methods such as centrifugation or filtration, is an highly energy intensive and thus is too expensive for low valued products like biodiesel [12]. Microalgal biomass recovery from the growth medium accounts almost 20–30% of biomass production cost [13]. Being cost effective and comparatively easy, chemical

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coagulation and flocculation are the preferred techniques for harvesting of microalgae [14,15]. Cationic flocculants neutralize the charge of an algal cell wall, thus promoting aggregation of flocculants with algal cells forming aggregates which settle via gravitational forces [11]. The efficiency of flocculation varies with the nature of flocculants, microalgal species and their charge densities, cell density, growth phase, pH and salinity of the medium etc. [11]. Moreover the choice of flocculant(s) is also based on the targeted end product of algal biomass [11]. Inorganic polymers such as ferric chloride and alum has limited use due to contamination of biomass as well as resulting wastewater [15]. Some flocculants also adversely affect the biochemical constituents such as carbohydrates, fatty acids and proteins of the microalgae thereby contaminating biomass which cannot be used for human or animal consumption [16]. Natural polymers such as guargum, moringa and chitosan have shown some promising results and do not contaminate biomass, however these are comparatively very expensive [3,17,18].

Pre-concentration of microalgal biomass with aid of suitable flocculants reduces the energy demand, and thus the overall cost of the harvesting [19,20]. Much research has been conducted into the design and development of various types of anionic, cationic and non-ionic synthetic polymers and co-polymers with varying molecular weight and charge densities for various types of water and wastewater applications including microalgal flocculation. These polymers act primarily through physical binding with the microalgal cells however, binding is greatly depend on the molecular weight and charge density of the polymer [21,22]. Earlier studies have been conducted on commercially available polyelectrolytes, organic or inorganic flocculants and have assessed mainly algal flocculation only [23–26]. Polyamine based cationic polyelectrolytes are one of the most widely used flocculants for water and wastewater treatment applications [21,27–29], however literature on the harvesting of microalgal biomass using such polymers is scanty. The present study was carried out to develop high molecular weight cationic polymer for microalgal harvesting. The novelty of our studies lies in the in situ design and development of high molecular weight cationic flocculant, its characterization and evaluation of its microalgal flocculation efficiency as well as an assessment of its effect on the lipid yield and profile of harvested microalgal biomass. In the present study, we designed and developed a high molecular weight cationic polymer by polycondensation of epichlorohydrin, N,N-diisopropylamine and ethylenediamine. The performance of this polymer as microalgal flocculant was evaluated using *Scenedesmus* sp. grown on BG11 medium in open circular pond. The major advantage of developing this type of cationic polymer is the high cationicity and hydrophilicity due to the presence of positively charged quaternary amines, which may improve the neutralization of negative charges of algal cell walls and facilitate adsorption bridging and thus flocculation. Chemical flocculants may influence the downstream processing such as lipid extraction. The effect of lipid yield and fatty acid composition were assessed for polyamine polymer flocculated *Scenedesmus* sp. biomass and compared with natural polymer chitosan and inorganic flocculant alum.

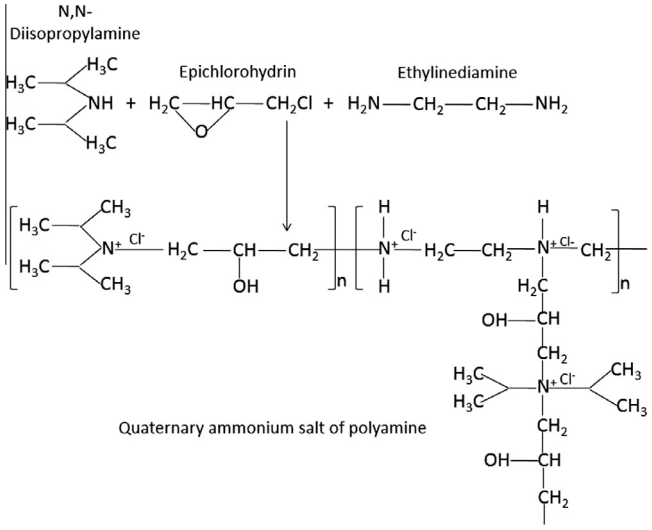
2. Materials and methods

2.1. Chemicals and reagents

Analytical grade epichlorohydrin, N,N-diisopropylamine, and ethylinediamine, purchased from Sigma Aldrich, was used in this study. Ultrapure water was used for the preparation of polymer solutions throughout the study.

2.2. Preparation of cationic polymer (quaternary ammonium salt of polyamine)

Epichlorohydrin (22.5 g) was first added to a 250 mL glass reactor at 30 °C initially equipped with a temperature controller and a mechanical stirrer. Thereafter then after 40 gm water along with 4 g of N,N-diisopropylamine was added to the reaction mass. N,N-diisopropylamine was used to reduce the gelling tendency during the polymerization reaction. Thereafter, ethylinediamine (15.5 g) was added by dropping it into the reactor with constant stirring to form highly viscous polymers at 70–75 °C. The reaction temperature was raised slowly to 85–90 °C and the reaction was



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