

Review Article

Chitosan and Its Derivatives Applied in Harvesting Microalgae for Biodiesel Production: An Outlook

Guanyi Chen,¹ Liu Zhao,¹ Yun Qi,¹ and Yuan-Lu Cui²

¹ School of Environment Science and Engineering, State Key Laboratory of Engines, Tianjin University, No. 92 Weijin Road, Nankai District, Tianjin 300072, China

² Tianjin State Key Laboratory of Modern Chinese Medicine, Tianjin University of Traditional Chinese Medicine, Tianjin 300193, China

Correspondence should be addressed to Yun Qi; qiyun@tju.edu.cn

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Although oil-accumulating microalgae are a promising feedstock for biodiesel production, large-scale biodiesel production is not yet economically feasible. As harvesting accounts for an important part of total production cost, mass production of microalgae biodiesel requires an efficient low-energy harvesting strategy so as to make biodiesel production economically attractive. Chitosan has emerged as a favorable flocculating agent in harvesting of microalgae. The aim of this paper is to review current research on the application of chitosan and chitosan-derived materials for harvesting microalgae. This offers a starting point for future studies able to invalidate, confirm, or complete the actual findings and to improve knowledge in this field.

1. Introduction

Fossil fuels currently account for about 80% of global energy production. As demand for energy continues to increase, oil prices will rise and fossil fuels will be exhausted at some point in the future. Meanwhile, extensive utilization of fossil fuels has led to adverse effects including global climate change, environmental pollution, and public health problems [1].

Therefore, many countries have started to take series of measures to resolve this problem [2]. Identifying alternative renewable sources of fuel that are carbon neutral is important for many countries. Among the potential sources of renewable energy, biodiesel is of particular interest. Major advantages of biodiesel include mitigation of carbon dioxide emissions and potential use as a substitute for petroleum [3]. Biodiesel also has a higher energy density than competing biofuels measured in kilojoules per unit of mass. Furthermore, widespread adoption of biodiesel could improve urban air quality as emissions of carbon monoxide and volatile organic compounds are significantly lower than petroleum-derived diesel. Biodiesel may become a primary energy source for sustainable development and could play a crucial role in the global energy infrastructure in the future. Energy

security may drive biodiesel production as nations attempt to reduce their reliance on petroleum imports.

More than 95% of biodiesel sources are first generation agricultural edible crop oils [4] such as palm oil, oilseed rape, and soybean. However, these vegetable oils are also used for human consumption, which may lead to an increase in price of food-grade oils. Meanwhile, any transition to biodiesel production based upon these crops would require arable land, with a corresponding drop in other forms of agricultural productivity. In theory, it should be possible to produce low-cost biodiesel using nonedible oils (second generation biofuels), such as frying oils, animal fats, soap stocks, and grease. However, these nonedible oils are rarely available in quantities suitable for industrial-scale biodiesel production [5]. As a consequence, there is renewed interest in methods of producing biodiesel from microalgae.

As a promising feedstock for biodiesel production, microalgae offers compelling advantages compared to other oil crops: (1) the cultivation of microalgae does not need much land as terraneous plants [6]; indeed, biomass growth might not require any arable land at all if offshore farming proves feasible [7]; (2) microalgae have much higher biomass productivities than land plants; (3) some microalgae species

are rich in oils; they can accumulate up to 20–50% (w/w DW) triacylglycerols [8] and certain strains may have content as high as 85% lipid under limited condition [9]; (4) microalgae utilize CO₂ from the atmosphere via photosynthesis, offsetting greenhouse gas emissions; (5) microalgae require less freshwater for cultivation than terrestrial crops. Microalgae growth effectively removes nutrients, such as nitrogen and phosphorus, and heavy metals from wastewater; (6) biodiesel produced from microalgal oil has advantageous properties compared to standard biodiesel. These advances suggest that industrial production of biodiesel from microalgal oils may be feasible in the near future.

2. Microalgae Harvest Strategy

Although oil-accumulating microalgae are a promising feedstock for biodiesel production, large-scale biodiesel production is not yet economically feasible. This is mainly due to the high-energy inputs required for harvesting [10]. However, as microalgae diameters are often as small as 3–30 μm, harvesting the microalgae is a significant problem. In some commercial production systems, the culture broths are below 0.5 kg/m³ dry biomass, which means that huge volumes need to be handled before algae oil can be extracted. Molina et al. estimated that harvesting can account for 20–30% of the total production cost [11]. Chisti even reported that the cost of the recovery process in his study contributed about 50% to the final cost of oil production [6].

Consequently, mass production of microalgae biodiesel acquires efficient low-energy harvesting strategy so as to make biodiesel production economically feasible. Microalgae can be harvested by centrifugation, filtration, flotation, sedimentation, and electrophoresis techniques [12].

Centrifugation can recover most microalgae from the liquid broth and is used in many commercial systems. Although centrifugation is effective, this process is energy intensive [13], which reduces the net energy return on investment (EROI) from the biodiesel produced from the microalgae, making this option less attractive both in financial and environmental terms. Norsker et al. calculated centrifugation required as much as 50% of the available energy in the recovered biomass [14]. From an energetic point of view, harvesting a large amount of microalgae using centrifugation is time consuming and costly [15]. Filtration is another option for harvesting cells, but this technology is only useful for the harvest of large species such as *Spirulina* but fails to recover small microalgae such as *Chlorella* or *Scenedesmus* [10].

Coagulation/flocculation processes offer high microalgae biomass recovery at reasonable costs [16]. These harvesting techniques have been successfully used in aquaculture, wastewater treatment, and removal of microalgae [10] and also reduce the net energy input required to produce biodiesel from microalgae feedstock.

Several flocculants have been developed to induce flocculation of microalgae cells that can be applied to the treatment of large amount of microalgae. According to their chemical compositions, there are two classifications of flocculants: inorganic flocculants and organic flocculants/polyelectrolyte flocculants [1].

The commonly used inorganic flocculants include ferric chloride (FeCl₃), aluminum sulfate (Al₂(SO₄)₃), and ferric sulfate (Fe₂(SO₄)₃) [17]. These multivalent metal salts are effective flocculants or coagulants and have been widely used to flocculate algal biomass. prepolymerized metal salts (such as polyaluminium chloride and polyferric sulfate) have proved to be efficient over a wider pH range [18]. However, flocculation by metal salts is not an appropriate method for cheap and sustainable harvesting of microalgae in large-scale microalgae culture. This is because these flocculants are expensive and may produce large amounts of sludge, which can kill or prevent the growth of the microalgae and leave a residue in the water, and the excess cationic flocculant needs to be removed before it can be reused [19]. Another disadvantage of metal salts as flocculants is the concern about the human health, such as involvement in Alzheimer's disease and carcinogenesis [20–22].

The organic flocculants, such as synthetic polymeric flocculants and modified natural polymers, have also been applied to the microalgae harvesting process. In the last few decades, chitosan has emerged as a favorable flocculating agent in harvesting microalgae. Chitosan is becoming increasingly important as a natural biopolymer due to its unique combination of properties like biodegradability, biocompatibility, renewability, bioactivity, and ecological acceptability, in addition to attractive physical and mechanical properties [23]. It also has variety of current and potential applications in wastewater treatment [24], biomedical engineering [25], food processing [26], and so forth. In particular, chitosan has also been examined to formulate nanoparticles to facilitate targeting drug to specified organ [27].

3. General Aspects of Chitosan

Chitosan, poly-β(1-4)-2-amino-2-deoxy-d-glucopyranose, is a cationic polyelectrolyte obtained by deacetylation of chitin. Chitin and chitosan are both aminoglucopyrans composed of N-acetylglucosamine (GlcNAc) and glucosamine (GlcN) residues. The chemical structures of chitin and chitosan are shown in Figure 1 [28]. Acetamide group of chitin can be converted into amino group to give chitosan, when the degree of deacetylation of chitin reaches about 50% (depending on the origin of the polymer). Chitosan is also polyelectrolyte which has several million Daltons. The average molecular weight of commercially available chitosan ranges between 3800 and 20,000 Daltons and is 66% to 95% deacetylated. The chitosan toxicity tests showed that the toxicity was negligible [29]. Because chitosan can be produced in various forms such as powder, paste, film, and fiber, it is more widely applied in industry than chitin [30].

Due to the presence of three different polar functional groups (–OH, –NH₂, and C–O–C), chitosan has high water capacity [28]. Chitosan has the special quality of gelling upon contact with anions, forming beads under very mild conditions [31]. And the presence of amino groups makes chitosan a cationic polyelectrolyte (pKa = 6.5), one of the few found in nature [32]. Ordinary chitosan is insoluble in water at near neutral pH and most common organic

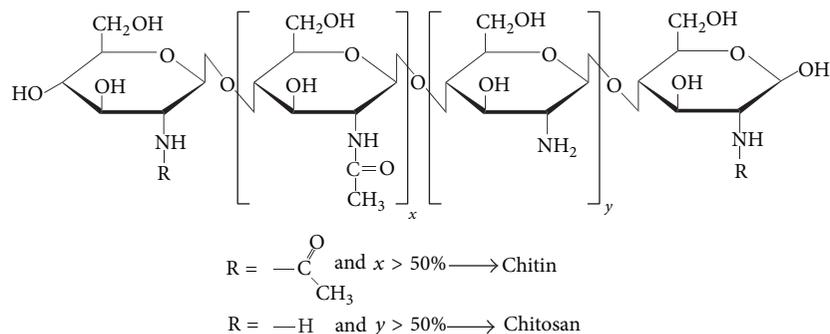
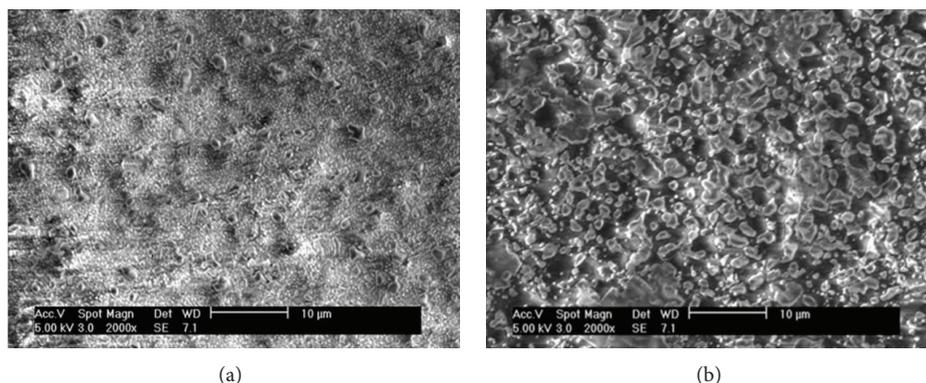


FIGURE 1: Structures of chitin and chitosan [28].

FIGURE 2: (a) SEM of *C. vulgaris* before harvesting. (b) SEM of *C. vulgaris* after harvesting [38].

solvents (e.g., DMSO, DMF, NMP, organic alcohols, and pyridine), which is attributed to extensive intramolecular and intermolecular hydrogen bonding between the chains and sheets, respectively [33]. Chitosan can be soluble in some diluted organic acids (such as acetic, formic, and lactic acids) and some inorganic acid. Although the distribution of acetyl groups along the chain may modify solubility [34], the solubilization is mainly due to the protonation of NH_2 groups on the C_2 position of the β -glucosamine unit.

4. Chitosan Applied in Harvesting Microalgae

Chitosan not only has been proved highly effective for water treatment and environmental protection, but also shows interesting properties in removing both freshwater algae and marine algae.

The most likely mechanisms involved in this coagulation are adsorption and charge neutralization. Chitosan has a net positive charge because of the high charge density of the chitosan. As the overall charge of microalgae cells is negative, the positively charged chitosan is strongly adsorbed on microalgae cells, which results in most of the charged groups being close to the surface of the cells [35] and effectively destabilize the microalgae [36]. Chitosan first neutralizes charges on the microalgae cells, weakens the electrostatic repulsion between the microalgae cells, and then reduces the interparticle repulsion. Such effect is called charge neutralization [37].

Some authors report chitosan as an effective algal flocculant. Figure 2 shows the scan electron microscope (SEM) of *Chlorella vulgaris* before and after flocculation by chitosan. After flocculation, *C. vulgaris* algae were surrounded by chitosan, and the surface became fibrillar. This change of surface was observably caused by chitosan, which possesses heterogeneous surface structure [38].

Using life cycle assessment (LCA), Beach compared the chitosan method to centrifugation and filtration/chamber press methods [39]. Figure 3 showed the system used as a basis for the comparison, where the cultivation and downstream were assumed to be equivalent among all methods. LCA showed that flocculation by chitosan for harvesting *N. oleoabundans* is the least energy intensive and had the best profile across all other categories of environmental impacts.

4.1. Effect of Chitosan Dosage on Flocculation Efficiency. In general, chitosan can effectively flocculate algal species at 5 mg/L to 200 mg/L. Divakaran and Sivasankara Pillai [40] reported that chitosan successfully removed 90% of turbidity with chitosan concentration of 5 mg/L. Ahmad et al. [41] reported a $99.0 \pm 0.4\%$ of *Chlorella* sp. removal at 10 ppm of chitosan. In order to obtain 95–100% flocculation efficiency, chitosan concentration was about 20 mg/L for *Chlorella* and 2 mg/L for *S. Costatum* [16]. Chitosan is required in low dosage in freshwater but its flocculating power is reduced in salt water.

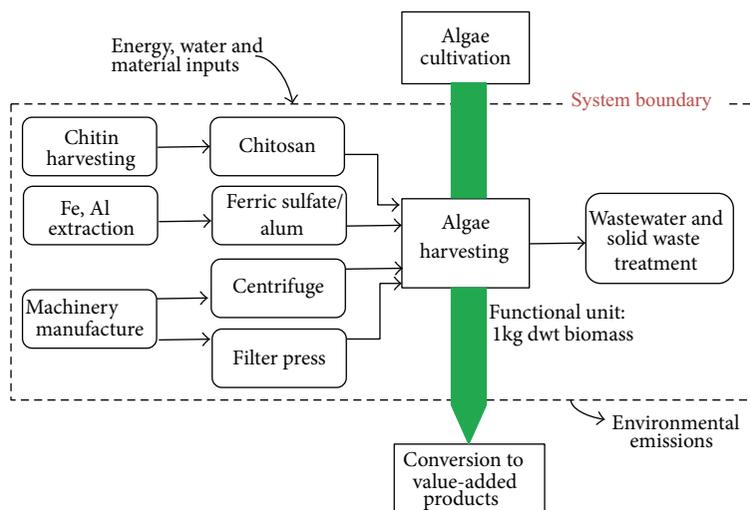


FIGURE 3: Overview of the system used as a basis for the comparison [39].

Chitosan's ability to remove microalgae effectively at low dosage is partly caused by its' properties. Chitosan not only acts as an adsorbent, but also spontaneously coagulates to agglomerate the microalgae cells. However, when using overdose of chitosan, the percentage of microalgae cells removed declined sharply, which may be caused by charge neutralization and bridging phenomena. During the flocculation, cationic charge of chitosan attracts the negatively charged microalgae, reducing the electrostatic repulsion among microalgal cells and then forming the flocs. Excess amino group led to restabilization of the microalgae and decreasing of separation efficiency [38].

4.2. Effect of pH on Flocculation Efficiency. The importance of pH on flocculation of microalgae was investigated by many researchers [41–44]. The influence of pH on chitosan's molecular structure can be due to differences in the protonation of the biopolymer amine groups and variations in the conformation of the macromolecule chain and in the structure of the flocs [37]. In alkaline solutions, the positive charge gradually disappeared and chitosan is able to produce large and dense flocs. When the pH increases to neutralization point, the algal cells have the highest negative charge, and the flocculation efficiency is enhanced as the electrostatic interaction between the algal cells and chitosan, whereas, in acidic solutions, chitosan becomes a more extended chain and therefore produces smaller looser flocs [20]. In the study of Divakaran and Sivasankara Pillai [40], maximum clarification was obtained at pH 7 for the freshwater species. Cheng et al. reported that a higher pH at 8.5 was optimal for *Chlorella sorokiniana* [42]. In the study of an even higher pH at 9.9, 90% of *Phaeodactylum tricornutum* was harvested with 20 ppm chitosan [18].

Morales suggested that chitosan activity and flocculation efficiency were increased as the viscosity and the mean surface charge of algal cells were decreased when pH was below 7 [16]. While Xu et al. reported that when the working

pH was at 6 or 5, half the amount of chitosan was needed to induce effective flocculation compared to pH 7 [43].

These differences in response to pH can be explained by difference in culture media, growth conditions, and unique strain properties, such as cell morphology, extracellular organic matter, and cell surface charge [44].

4.3. Effect of Algae Species on Flocculation Efficiency. The flocculation efficiency of algal suspension is different from one algal species to another. *Chlorella vulgaris* reached 99.7% removal rate at 200 mg/L chitosan [45]. While 150 mg/L of chitosan was required for optimal flocculation of *Chaetoceros muelleri* [46]. For *Skeletonema costatum* 2 mg/L of chitosan was needed when 95% flocculation efficiency was obtained. Optimal flocculation of some species was list in Table 1.

5. Chitosan Modified Flocculants and Their Flocculation Efficiency

Chitosan exhibits limitations in its reactivity and process ability. For a breakthrough in utilization of chitosan in flocculation of microalgae, chitosan modification to introduce a variety of functional groups will be a key point. Chitosan can be modified by chemical or physical processes to improve the mechanical and chemical properties. The efficiency of adsorption depends on physicochemical properties, mainly surface area, porosity, and particle size of adsorbents. As such procedure would not change the fundamental skeleton of polymers, chitosan would keep its original physicochemical and biochemical properties and finally would bring new or improved properties [47]. A great number of chitosan derivatives have been obtained by grafting new functional groups on the chitosan backbone to increase adsorption capacity. The new functional groups are incorporated to increase the density of sorption sites, to change the pH range for sorption, and to change the sorption sites in order to increase sorption. The chemical modification affords a wide range of derivatives

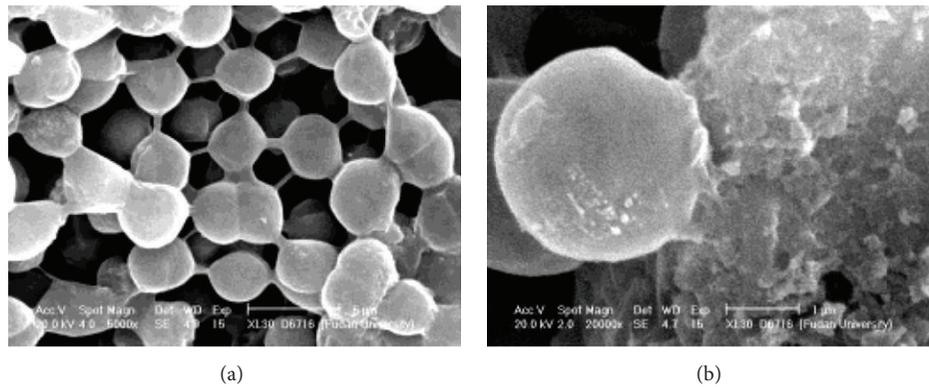


FIGURE 4: SEM images of algae treated with chitosan modified adsorbent [53].

TABLE 1: Optimal flocculation of some microalgae.

Species	Chitosan dosage	Parameters	Flocculation efficiency	References
<i>Chaetoceros calcitrans</i>	80 mg/L	pH 8.0	80%	[46]
<i>Chaetoceros muelleri</i>	150 mg/L	pH 8.0	95%	[46]
<i>Chlorella</i>	5.0 mg/L	pH 7.0,	90%	[63]
<i>Chlorella consortium</i>	25 mg/L	Stirring for 1 min, settling for 10 min	58 ± 8	[10]
<i>Chlorella sorokiniana</i>	10 mg/gram algal dry weight	pH 6	99%	[43]
<i>Chlorella sorokiniana</i>	25 mg/L	Stirring for 1 min, settling for 10 min	30 ± 11	[10]
<i>Chlorella</i> sp.	10 ppm	Mixing for 20 min, mixing at 150 ppm, and sedimenting for 20 min	99.0 ± 0.4%	[41]
<i>Chlorella vulgaris</i>	200 mg/L	In a logarithmic growth phase	99.7%	[45]
<i>Chlorella vulgaris</i>	30 mg/L	pH 8.7, 300 rpm, and settling for 10 min.	92%	[38]
<i>Chlorella vulgaris</i> and <i>Microcystis</i> sp.	214 mg/L	Fish-processing wastewater, agitation speed of 131 rpm	91.9%	[64]
<i>Chlorococcum</i> sp.	25 mg/L	Stirring for 1 min, settling for 10 min	38 ± 1	[10]
<i>Nannochloropsis</i> sp.	100 mg/L	pH 9.0	92%	[62]
<i>Neochloris oleoabundans</i>	100 mg/L	Mixing time for 10 min, mixing rate of 350 rpm	95%	[39]
<i>Pavlova lutheri</i>	80 mg/L	pH 8.0	80%	[46]
<i>Phaeodactylum tricoratum</i>	20 mg/L	pH 9.9 Settling time of 10 min	92%	[18]
<i>Scenedesmus costatum</i>	2 mg/L	pH 7	95–100%	[16]
<i>Scenedesmus obliquus</i>	25 mg/L	Stirring for 1 min, settling for 10 min	20 ± 15	[10]
<i>Scenedesmus quadricauda</i>	10 mg/L	pH 8.0; SDS was used as the collector	90%	[65]
<i>Skeletonema costatum</i>	80 mg/L	pH 8.0	70%	[46]
<i>Synechocystis</i>	15 mg/L	pH 7.0	>90%	[63]
<i>Tahitian Isochrysis</i>	40 mg/L	pH 8.0	90%	[46]
<i>Tetraselmis chui</i>	40 mg/L	pH 8.0	80%	[46]
<i>Thalassiosira pseudonana</i>	40 mg/L	pH 8.0	90%	[46]

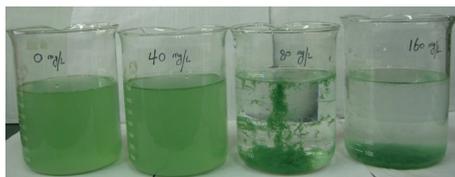


FIGURE 5: Flocculation character of CMK and *M. aeruginosa* NIES-843 at different CMK loading levels [54].

with modified properties for specific use and applications in diversified areas mainly of pharmaceutical, biomedical, and biotechnological fields [32]. Such modification can also be applied to harvesting microalgae.

5.1. Chitosan Modified Soils. Chitosan modified by soil particles (including the silica sand and local soil) showed highly effective in flocculating algae cells [48–52]. Pan and coworkers found that local soil particles including sand were critical for speeding up the kinetic processes of flocculation and sedimentation of algal flocs. The polymeric netting and bridging function of chitosan were the key mechanisms that allowed local soil particles to quickly flocculate algal biomass. Chitosan modified adsorbent has the functions of both flocculation and adsorption. Figure 4(a) shows the function of bridging, while Figure 4(b) illustrates the function of adsorption [53]. The chitosan made a “net” that captured the algae cells and other particles, and the soils provided the ballast or mass to carry the aggregates to the bottom. Chitosan was also important in inhibiting the escape of cells from the flocs. Chitosan and polyaluminium chloride used together as modifiers make it possible to use local beach sand for harvesting microalgae in seawater [50].

Shao et al. studied the physiological responses of *Microcystis aeruginosa* under the stress of chitosan modified kaolinite (CMK). When flocculated with CMK, Chl a, carotenoids, phycocyanin, and allophycocyanin were much lower than the control. The results indicated that high level of CMK could cause cellular membranes damage and then the intracellular substances leakage and finally could cause the death of *M. aeruginosa* NIES-843 cell. Figure 5 showed that the strain can be effectively flocculated by CMK at 80 and 160 mg/L. However, the *Microcystis* cultures turned to be bluish at that time, which indicated the leakage of phycobilins [54].

5.2. Aluminum Chloride and Aluminium Sulphate Modified Chitosan Used as Flocculants

5.2.1. Aluminum Chloride Modified Chitosan. Chitosan could enhance the flocculation performance of polyaluminium chloride (PAC), when the high algae-laden water was treated by coagulation/flocculation/dissolved air flotation (C/F/DAF) [55]. The removal rate of algae cells was increased apparently compared with adding PAC alone. The structure and strength of flocs were improved when less than 1.0 mg/L chitosan was added, which significantly reduced the residual aluminum concentration.

Zhang et al. reported a composite coagulant (PACI-CTS), which was made of polyaluminium chloride and chitosan. When 21.0 mg/L of the coagulant is added, 98.15% turbidity, 67.78% COD, and 84.05% TP can be removed. This coagulant can be applied in the pretreatment of blue algae biogas slurry [56]. Figure 6 showed the SEM of PACI-CTS. PACI with certain crystal structure was embedded in chitosan, which enabled the composite coagulant to possess much more positive charge. When the PACI-CTS was added to the algal water, it can decrease the negative charge on the surface of microalgae and enhance the flocculation by polymer bridging.

5.2.2. Aluminium Sulphate Modified Chitosan. Wang et al. used aluminium sulphate and chitosan as coagulants to treat the high algae-laden water. The compound action of aluminium sulphate and chitosan can reduce dosage of aluminum salt coagulant for meeting the treatment requirements, which in turn reduces the residual aluminium in treated water. Moreover, with the coagulation aid of chitosan, the algae flocs were larger and more compact and had a faster settling velocity [57].

5.3. Fly Ash Modified Chitosan. The performance of activated fly ash modified chitosan (FA-MC) as a flocculant to remove *Microcystis aeruginosa* was reported by Qiao et al. [58]. 90% of algae can be removed at the dosage of 0.25 mg/L chitosan within 1 h or at the dosage of 0.35 mg/L chitosan within 40 min. The authors found that the algal extracellular organic matter had a priority to consumption of flocculant in initial period of flocculation. In the late stage of flocculation, extracellular organic matter can decrease the adsorption bridging and entrapping-weeping functions of fly ash modified chitosan.

5.4. Magnetic Chitosan. Ferroferric oxide modified with chitosan was used to remove algal in freshwater [59]. This magnetic polymer could remove over 99% algal cells, which is much more effective when comparing with chitosan or Fe_3O_4 alone. The author found that the high algal removal efficiency of magnetic polymer is due to the cooperation between chitosan and Fe_3O_4 particles. Chitosan can enhance the function of netting and bridging in flocculating algal cells, while the Fe_3O_4 could separate the flocculated algal cells from water by its high magnetic response in the presence of magnetic field. Figure 7 showed the SEM of algal cells that was captured by magnetic polymer. The network bridge of chitosan and the magnetic Fe_3O_4 agglomerated the cells. After flocculation, the algae cells were still kept in original shape, which indicated that the flocculant did not destroy the cells.

This technique has been successfully applied to pilot experiments in Chaohu Lake, China.

5.5. Nanochitosan. Nanoscaled chitosan particles are prepared by some researchers. Such chitosan-coated nanoparticles have overcome the limitation of microscaled particles

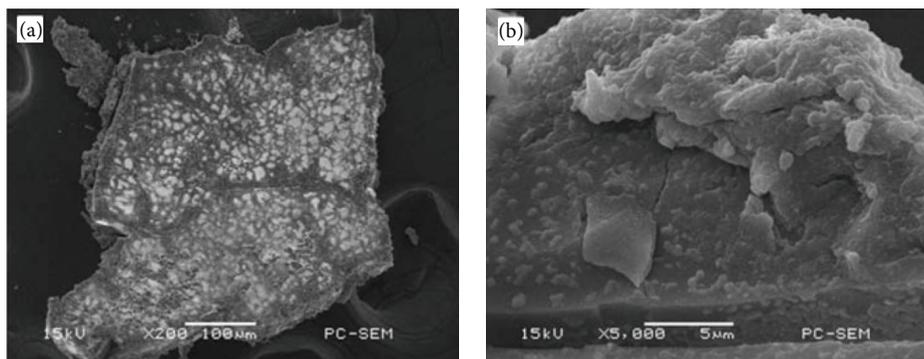


FIGURE 6: SEM of PACI-CTS [56].

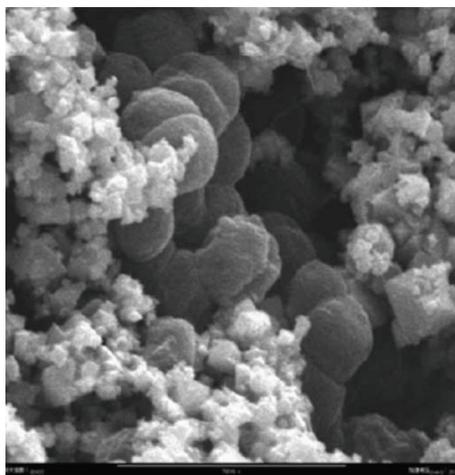


FIGURE 7: SEM images of the floccules of magnetic polymer algal cells ($\times 8,000$) [59].

by providing larger surface area. Owing to high adsorption capacity and stability, these particles can be used as adsorbents for food dyes adsorption [60], protein [61], and microalgae.

Farid et al. prepared chitosan nanopolymer using ionic gelation method, which added sodium tripolyphosphate to chitosan solution [62]. The average of particle size was 13.7 nm.

When nanochitosan was used as flocculant agent, the dosage of flocculant consumption decreased to 60 mg/L, while the optimum chitosan dosage was 100 mg/L for harvesting. The removal efficiency was about 98%, which increased by 9% when nanochitosan instead of chitosan was used. The author figured out that the nanochitosan had high harvesting rate because its particle had ions cross-linked with sodium tripolyphosphate. When chitosan is dissolved in water at acidic pH, it gives both hydrated amino group and $-\text{NH}_3^+$ ions. The sodium tripolyphosphate (STPP, $\text{Na}_5\text{P}_3\text{O}_{10}$) presents both hydroxyl and phosphoric ions in water. These phosphoric ions of STPP can interact with $-\text{NH}_3^+$ ions of chitosan, lead to crosslinking between chitosan and STPP, and result in big network of polymers, which adsorb microalgae and create a greater degree of bridging. In addition, the

nanosize particles increase the adsorption ability and contact surfaces.

The author also analyzed the cost of harvesting process. For production of 1 kg of dry biomass, harvesting process would cost about \$0.0246, which showed the feasibility of using nanochitosan as flocculation agent.

6. Conclusions

Flocculation using chitosan is becoming a promising alternative to replace conventional flocculants in removing/harvesting microalgae. Although chitosan itself can flocculate algae, the use of some modification process may improve the properties of chitosan. Arguments on which flocculant is better in harvesting microalgae are still going on as each of the flocculants has its own advantages and disadvantages. Due to the different experimental conditions, such as pH, microalgae species, and ionic strength, it is different to compare the low-cost flocculants. Meanwhile, more studies should transfer to industrial scale.

Conflict of Interests

The authors declare that there is no conflict of interests.

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