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Improvement of microalgae harvesting by magnetic nanocomposites coated with polyethylenimine

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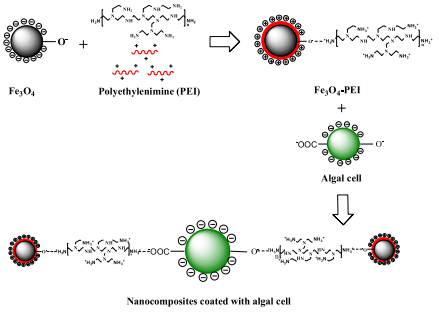
HIGHLIGHTS

- Fe_3O_4–PEI nanocomposites with large amount of —NH_2 groups were synthesized.
- 97% of harvesting efficiency for microalgal cells was obtained with the nanocomposites.
- Magnetic separation provides a powerful tool for microalgae harvesting in practice.

GRAPHICAL ABSTRACT



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ABSTRACT

Fe_3O_4 nanoparticles were functionally coated with polyethylenimine (PEI), which contained a high concentration of —NH_2 groups, for the efficient harvesting of microalgae. The functional magnetic nanocomposites were 12 nm in diameter and 69.77 emu/g of saturation magnetization. Using a nanocomposite dosage of 20 mg/L for harvesting *Chlorella ellipsoidea* cells, a harvesting efficiency of 97% was achieved within 2 min. Increasing the temperature resulted in an increase in harvesting efficiency. The adsorption isotherm data fit the Langmuir model, suggesting that the adsorption was monolayer. The adsorption capacity of the Fe_3O_4–PEI nanocomposites for the microalgal cells reached up to 93.46 g-DCW/g-nanocomposites through electrostatic attraction and nanoscale interactions between the nanocomposites and the microalgal cells. The functional nanocomposites provide a base for efficient microalgae harvesting with clear advantages such as rapid execution, low energy consumption, and improves water-use in the algal harvesting process.

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1. Introduction

The nanotechnology revolution has played an important role in the development of diverse fields including environmental remediation, wastewater treatment, consumer products, and the construction industry [1–4]. Magnetic nanoparticles, with their unique properties of superparamagnetism, have demonstrated potential applications in biological separation, drug delivery, hyperthermia treatment, and enzyme immobilization [5–7]. Magnetic nanoparticles can selectively adsorb a desired target, forming complexes that can be efficiently and rapidly recovered using an external magnet [8].

Microalgae offer a wide range of potential commercial applications in food supplements, animal feed, environment remediation, and biofuel production [9,10]. Biofuels produced from microalgal biomass have advantages over petroleum-based oil because they are renewable, non-toxic, contain less sulfur, and are environmentally safe [11]. Obtaining oil from microalgal biomass generally involves several stages, including microalgal cultivation, biomass

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harvesting, dewatering and processing, and oil extraction [12]. Of these steps, the biomass harvesting accounts for at least 20–30% of the total production cost [13]. The harvesting of the microalgal cells continues to be a challenge due to their small cell size, their relatively low density in liquid medium, stable due to surface charge, and the requirement for large volume of water for processing [14]. Techniques for harvesting microalgae have been developed, including centrifugation, flocculation, filtration, sedimentation, flotation, and electrophoresis; however, these methods are associated with economic and technical drawbacks such as high cost and/or energy usage, and complicated methods of operation [15].

Magnetic separation is a simple method that has been used for the recovery of microalgal cells. For example, an *in situ* magnetic separation method for the recovery of both freshwater and marine microalgae with naked Fe_3O_4 nanoparticles has been previously developed and studied [16,17]. Fe_3O_4 nanoparticles have been modified with different agents to improve the efficiency of microalgal harvesting, such as diallyldimethylammonium chloride surface coat on Fe_3O_4 nanoparticles for the magnetophoretic separation of *Chlorella* sp., which achieved a removal efficiency of 99% [18]. In another study, silica-coated magnetic particles for the separation of both freshwater and marine algae achieved a separation efficiency of 95% [19]. However, the cost of magnetic nanoparticles for microalgae harvesting remains high due to their low recovery capacity. It is therefore imperative to develop a simple and effective method using nanomaterials that have a high recovery capacity and low dosage requirement by integrating the advantages of magnetic separation with the surface properties of microalgal cells.

The surface characteristics of microalgal cells play a key role in the recovery performance. Using titration measurements, Zhang et al. found that the microalgal cell surface contains carboxyl, phosphate, amine, or hydroxyl groups [20]. Lim et al. measured the electrophoretic mobility, which provides an indication of the surface charge properties, and found that there was an increase in electronegativity during cultivation [18]. Therefore, an understanding of the structure, functional groups, morphology, and charge of microalgal cells is a key element in the design and synthesis of functional magnetic nanoparticles for efficient harvesting [21].

Polyethylenimine (PEI), which is known for its high density of positive charge, was introduced onto the surface of Fe_3O_4 nanoparticles to bring in cationic charge on the Fe_3O_4–PEI nanocomposites. The magnetic nanocomposites were characterized and applied to harvest freshwater microalgae *Chlorella ellipsoidea*. Several key operational parameters that affect the harvest process were investigated, the Langmuir and Freundlich models were used to describe the equilibrium isotherms, and the adsorption mechanism of the Fe_3O_4–PEI nanocomposites onto the microalgal cells was elucidated. In addition, the reusability of the culture medium after magnetic separation was evaluated for repeated microalgal growth in order to achieve improved water-usage in the microalgal cultivation and harvesting process.

2. Materials and methods

2.1. Synthesis of Fe_3O_4–PEI nanocomposites

To synthesize Fe_3O_4 nanoparticles, 0.99 g $FeCl_2{\cdot}4H_2O$ and 2.7 g $FeCl_3{\cdot}6H_2O$ were dissolved in 100 mL distilled water in a four-neck flask vessel and vigorously stirred at 80 °C under a nitrogen atmosphere. After the addition of 10 mL NH_4OH (25 wt.%) and continuous stirring for 30 min, the precipitated magnetite was separated from the solution using a small permanent magnet and washed four times with distilled water. The Fe_3O_4 nanoparticles were then mixed with a PEI solution (molecular weight of 1.2 kDa) and dissolved in a phosphate buffer (pH 7.3) at a volume ratio of 1:9 to get Fe_3O_4–PEI nanocomposites [22]. The concentration of the resulting magnetite nanocomposites in the mixed system was 0.005 vol.%, and the mixture was stirred for approximately 1 h at 25 °C to ensure sufficient interaction between the PEI and the Fe_3O_4 nanoparticles. The Fe_3O_4–PEI nanocomposites were then collected magnetically, washed three times with distilled water to remove the excess PEI, and the Fe_3O_4–PEI nanocomposites were dispersed in distilled water for further use.

2.2. Microalgae source and cultivation

C. ellipsoidea used in this study was stored at the Institute of Process Engineering, at the Chinese Academy of Sciences. The strain was cultivated in 100 mL BG-11 liquid medium in a 250 mL Erlenmeyer flask on a rotary shaker (100 rpm). The initial microalgal biomass was 0.077 g dry cell weight (DCW)/L. The cultures were illuminated at 35 μmol m^{-2} s^{-1} on a light/dark cycle of 16 h/8 h at 25 ± 1 °C.

2.3. Microalgae harvesting and medium reuse

Microalgae were harvested by thoroughly mixing the Fe_3O_4–PEI nanocomposites with the microalgal culture for 2 min at 120 rpm in Erlenmeyer flasks. The microalgal cells were coated with the nanocomposites, and a small permanent magnet ($Nd_2Fe_{14}B$, 2000 G, Hiway electrical Co., Ltd.) was used to separate the Fe_3O_4–PEI coated algal cells at the sides of the Erlenmeyer flasks from the mixture. To test the effect of growth stage on magnetic microalgae harvesting, the microalgal cultures were harvested using Fe_3O_4–PEI nanocomposites at different growth periods. The recovery capacity was calculated when a 95% harvesting efficiency was achieved. To determine the optimal pH and nanocomposite dosage, different doses of Fe_3O_4–PEI nanocomposites were used for microalgae separation at different pH values and the recovery capacities were calculated.

In order to estimate the reusability of the medium after harvesting, the culture supernatant was reused 10 times. The Fe_3O_4–PEI nanocomposites were washed five times with sterilized water before they were used for harvesting the microalgal cells, and all operations were conducted using sterile techniques. The concentrations of the essential nutrients NO_3- and PO_4^{3-} were tested in the collected medium after each harvest and supplemented to achieve the initial concentration of the BG-11 medium. The strain was taken from solid medium and pre-cultured in 100 mL fresh liquid medium in a 250 mL Erlenmeyer flask for 14 days. The pre-cultivated microalgal cells were used as inoculums in order to start each culture with the same initial microalgal biomass each time. Harvesting using Fe_3O_4 nanoparticles and the centrifugation method (8000 rpm, 10 min) were used for comparison. All cultivations were conducted in triplicate, incubated for 14 days, and the final biomass density was measured.

2.4. Analytical methods

To measure the dry cell weight (DCW), the microalgal samples were diluted or concentrated to various concentrations and the optical densities (680 nm) were measured. The samples were then collected by centrifugation (10,000 rpm, 5 min) in pre-dried and pre-weighed centrifuge tubes, washed three times with distilled water, and dried to a constant weight at 105 °C for 48 h. The biomass concentration was then calculated based on the linear correlation between the optical density and DCW [23,24].

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