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Research article

In-situ self-assembly of plant polyphenol-coated Fe_3O_4 particles for oleaginous microalgae harvesting

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ABSTRACT

Plant polyphenol (PP), a natural polymer from the *Larix gmelinii*, was selected as the surfactant to synthesize Fe_3O_4. The Fe_3O_4-PP composite was prepared by *in-situ* self-assembly in solvothermal synthesis, and characterized using FE-SEM, TEM, XRD, FTIR, XPS, TGA, and VSM. The harvesting efficiency of *Chlorella vulgaris* was investigated under different parameters, including algal organic matter, dosage, and pH. The results showed that the core-shell sphere of Fe_3O_4-PP (~150 nm) was coated by ~50 nm PP with a saturated magnetization of 40.0 emu/g. The Fe_3O_4-PP could be directly applied to the culture broth (1.5 g dry cell weight/L, pH = 9.03), achieving 93.0% of harvesting efficiency at 20 g/L. Cells were detached from the harvested aggregates by adjusting pH value to 9.80 and with ultrasonication, which achieved 95.6% of recovery efficiency. The recycled Fe_3O_4-PP showed high stabilities in surface properties, maintaining more than 87.5% of harvesting efficiency after five recycles.

1. Introduction

The demand for alternative energy sources is continually increasing due to environmental issues such as climate change caused by the combustion of fossil fuels (Guldhe et al., 2017). Microalgal biofuels have potential application prospects as a fossil fuel alternative, as they are renewable, nontoxic, have low land requirements and high production rates (Carneiro et al., 2017). One of the most crucial factors limiting the industrial application of microalgae, is the high costs associated with the harvesting step (Tandon and Jin, 2017).

The traditional harvesting techniques include sedimentation, flocculation, centrifugation, filtration, flotation, and electrophoresis (Wang et al., 2015). Compared with these techniques, magnetic harvesting is a newly emerging and noticeable method, due to its relatively simple operation, high treatment capacity, low costs, and low energy consumption (Toh et al., 2014a). During the magnetic harvesting processes, microalgae cells tagged by magnetic particles develop into magnetic aggregates because of surface interaction between the cells and particles. Aggregates are then attracted to a magnetic field, resulting in separation of microalgae from the original solution (Ge et al., 2015). In comparison, naked Fe_3O_4 particles are extremely unstable and tend to aggregate rapidly due to both van der Waals and magnetic attraction among particles, causing aggregation and lower surface energy (Ditsch et al., 2005; Lim et al., 2009). The colloidal stability of Fe_3O_4, a central standard used to ensure effective virtual applications of magnetic particles, is promoted via surface modification of surfactants, inducing electrosteric repulsion among particles and overcoming attractive interactions (Runkana et al., 2006; Seebergh and Berg, 1994). The surface functionalized Fe_3O_4 have received many research attentions, and show great potentials in the application of microalgal harvesting (Wang et al., 2015). As shown in Table 1, the synthesis of surface functionalized Fe_3O_4 for microalgal harvesting, is generally performed using a two-step method where the naked Fe_3O_4 particles are prepared first by co-precipitation and then combined with the surfactant (Wang et al., 2014). However, the *in-situ* self-assembly is a common method used in the solvothermal synthesis to prepare the functionalized Fe_3O_4 particles (Aslam et al., 2017; Ji et al., 2017). This method uses the chemical reaction of iron precursors and surfactant together under a certain temperature (100–1000 °C) and pressure (1–100 MPa) (Byrappa and Yoshimura, 2001; Wong et al., 2011; Zhi et al., 2006). The solvethermal synthesis can maintain a higher continuous nucleation rate and better particle size distribution, than with co-precipitation, by controlling parameters such as pressure, temperature, reaction time, and

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Table 1
Comparison on surface functionalized Fe_3O_4 particles in microalgae harvesting.

Magnetic particle	Surfactant	Method	Algal specie	Algal biomass	Culture media	Dosage (mg/L)	Harvesting efficiency	Separation time (min)	Recycle method	Reference
Porous-Fe_3O_4@PA	Poly-arginine (PA)	Chemical precipitation	*Chlorella* sp. HQ	0.2 g/L	Selenite enrichment medium	10–50	95% pH 8.0	20	Strong base and ultrasonication	(Liu et al., 2017)
CS-OTES-MNP	Octyltriethoxysilane (OTES) and cationic surfactants (CS)	Co-precipitation	*Chlorella* sp. KR-1	1.3–1.5 g/L	Modified N8 medium	598–690	96.6%	1	Sodium dodecyl sulfate and ultrasonication	(Seo et al., 2016)
SF-IONPs	Poly (diallyldimethylammonium chloride) (PDDA)	Chemical precipitation	*Chlorella* sp.	3.0×10^{10} cells/L	Suspended in deionized water	198	98.89%	6	–	(Toh et al., 2014a)
SF-IONPs	Chitosan powder	Chemical precipitation	*Chlorella* sp.	3.0×10^{10} cells/L	Bold's basal medium	300	95.61%	20	–	(Toh et al., 2014b)
PEI-coated MNPs	Polyethylenimine (PEI)	Chemical precipitation	*Scenedesmus dimorphus*	0.8 g/L	Modified bold's basal medium	60–120	83–91% pH 7.0	3	Ultrasonication and recoating with PEI	(Ge et al., 2015)
Fe_3O_4@PAMAM	Amino-riched polyamidoamine (PAMAM)	Chemical coprecipitation	*Chlorella* sp. HQ	0.2 g/L	Selenite enrichment medium	80	95% pH 8.0	2	Strong base and ultrasonication	(Wang et al., 2016)
CPAM-Fe_3O_4	Cationic polyacrylamide (CPAM)	Chemical coprecipitation	*Botryococcus braunii*	1.8 g/L	Blue-green medium (BG-11)	25	>95% pH 7.0	10	–	(Wang et al., 2014)
CPAM-Fe_3O_4	Cationic polyacrylamide (CPAM)	Chemical coprecipitation	*Chlorella ellipsoidea*	0.7 g/L	Blue-green medium (BG-11)	120	>95% pH 7.0	10	–	(Wang et al., 2014)

Note: SF-IOPs, surface functionalized iron oxide nanoparticles.
MNPs, magnetic nanoparticles.
–, not mentioned.

precursor concentration (Wang et al., 2010, 2012b).

Natural surfactants as well as synthetic surfactants are applied in solvothermal synthesis of Fe_3O_4 particles, such as chitosan, polyethylene glycol diacid, polyethyleneimine, and poly (acrylic acid) (Park et al., 2008; Shen et al., 2014; Wang et al., 2013c; Zhou et al., 2013). Surfactants are characterized by their polar and hydrophilic groups, including carboxylic acid, amidogen, hydroxyl, and ether bonds. The functional groups not only control the nucleation and growth processes of Fe_3O_4 particles to realize different size and size distribution, but also improve the electrostatic stabilization of the aqueous magnetite suspensions (Nguyen et al., 2014). Plant polyphenol (PP), also referred to as natural polyelectrolyte or tannin, is a natural anionic polymer that is extracted from the bark and wood of tree species such as, *Acacia*, *Castanea*, and *Schinopsis*, with a molecular mass ranging between 500 and 5000 Da (Martinez and Castaneda, 2013; Wang et al., 2013a). PP molecules possess multi-aromatic rings and different active functional groups, for instance, phenolic hydroxyl groups, hydroxyl groups, and carboxylic groups, which contribute to PP hydrophilicity, surface activity, and complexation ability (Martinez and Castaneda, 2013). Due to weak flocculation properties, PP can be applied as a coagulant aid for the capture of colloidal particles (Qin and Liu, 2006). In order to improve the cationic strength and be used as the coagulant, PP need to be modified via the *Mannich* reaction (Wang et al., 2013a). The modified PP achieved more than 90% separating efficiency of microalgae cells in both harvesting of oleaginous microalgae and removing of harmful microalgae (Mezzari et al., 2014; Wang et al., 2013a). However, the structure and property of abundant phenolic hydroxyl groups of PP have not been utilized in synthesis of Fe_3O_4 particles. Thus, PP is selected as a surfactant the first time to prepare Fe_3O_4 in this study, relying on the advantages of the hydrophilic functional groups. Meanwhile, the natural flocculation property of PP is utilized to harvest microalgae cells after successful coating on Fe_3O_4 surface.

In the present study, the Fe_3O_4-PP particles were synthesized through the *in-situ* self-assembly method in solvothermal synthesis. The characteristics of Fe_3O_4-PP were investigated. *Chlorella vulgaris* was selected as the model of oleaginous microalgae. The harvesting efficiency of *C. vulgaris* was studied under different algal organic matter (AOM), dosage, and pH conditions, with the mechanism of microalgae harvesting by Fe_3O_4-PP particles also discussed. The method of recycling Fe_3O_4-PP particles was assessed and the properties of recycled Fe_3O_4-PP particles were examined.

2. Materials and methods

2.1. Chemicals

The PP powder was extracted from the bark of *Larix gmelinii*, obtained from Inner Mongolia Forestry Industrial Co., Ltd. (Yakeshi, China), at a cost of 6000 CNY/ton. Ferrocene ($Fe(C_5H_5)_2$) was purchased from Shandong Xiya Reagent Co., Ltd. (Shandong, China). Tannic acid was purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Isopropanol, petroleum ether, ethanol, and chemicals used in culture media were supplied by the Beijing Chemical Works Co., Ltd. (Beijing, China). All reagents above were of analytical reagent grade and were applied without further purification. The KBr with spectroscopically pure grade was purchased from Fluka Chemicals Co. (Seelza, Germany).

2.2. Algae culture

Chlorella vulgaris (FACHB-31) was obtained from the Institute of Hydrobiology, Chinese Academy of Sciences (Wuhan, China). *C. vulgaris* was cultured in 500 mL Erlenmeyer flasks containing