ACS APPLIED MATERIALS & INTERFACES

Research Article

www.acsami.org

Magnetic Flocculant for High Efficiency Harvesting of Microalgal Cells

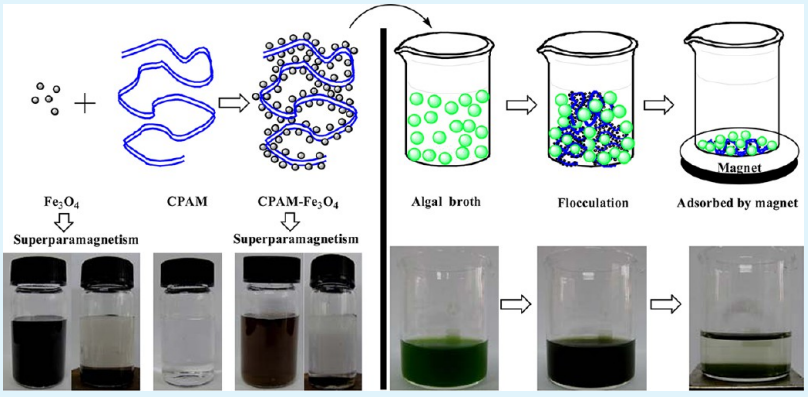
Shi-Kai Wang,[†,‡] Feng Wang,[†] Yi-Ru Hu,[†,‡] Amanda R. Stiles,[§] Chen Guo,*[,†] and Chun-Zhao Liu*[,†]

[†]National Key Laboratory of Biochemical Engineering & Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

[‡]University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

[§]Department of Plant and Microbial Biology, University of California, Berkeley, California 94720, United States of America

Supporting Information



ABSTRACT: Magnetic flocculant was synthesized for the highly efficient recovery of microalgal cells. The highest flocculation was achieved using the magnetic flocculant synthesized with iron oxide and 0.1 mg/mL cationic polyacrylamide (CPAM). This resulted in a recovery efficiency of more than 95% within 10 min using a dosage of 25 mg/L for *Botryococcus braunii* and 120 mg/L for *Chlorella ellipsoidea*. For both species, the adsorption isotherm data fit the Freundlich model better than the Langmuir model, indicating that the adsorption process was a heterogeneous multilayer. The maximum adsorption capacity was 114.8 and 21.4 mg dry cells/mg-particles at pH 7 for *B. braunii* and *C. ellipsoidea*, respectively. The primary flocculation mechanism was bridging, which was assisted by the electrostatic interactions between the microalgal cells and the magnetic flocculant under acidic conditions. These results provide new opportunities and challenges for understanding and improving the harvesting of microalgae using magnetic separation.

KEYWORDS: *microalgae harvesting, cationic polyacrylamide, magnetic flocculant, Botryococcus braunii, Chlorella ellipsoidea*

1. INTRODUCTION

Biodiesel derived from microalgae is a potential alternative to fossil fuels, and microalgae are regarded as the only source of renewable biodiesel that is capable of replacing traditional fossil fuels. This is due to several advantages of microalgae compared to other biodiesel feedstocks, such as a higher growth rate and oil content, the ability to be cultivated in non-arable areas, and the production of multiple types of lipids, hydrocarbons, and other complex oils.[1,2] *Botryococcus braunii* and *Chlorella ellipsoidea* are particularly good species for biofuel production. *B. braunii* can produce an unusually high hydrocarbon percentage, up to 75% of its dry biomass, and it also has a high CO_2 fixation rate. Chlorella can be cultivated under various types of conditions; it multiplies rapidly and has a high lipid content.[2,3]

Due to the dilute nature of microalgal cultures and their small cell size,[4,5] the harvesting and dewatering steps are difficult aspects for the industrialization of microalgal biofuels, and their combined operating costs contribute to 20−30% of the total production cost.[6,7] Of several traditional microalgal cell harvesting methods,[8] flocculation can markedly decrease the harvesting costs and energy demand.[9] The flocculation of microalgae can be achieved using a variety of flocculants, such as metal salts, organic polymers, and natural biopolymers. Metal salts are widely used in the flocculation process; however, the harvested biomass often contains high concentrations of metals that influence the downstream processing or the ultimate application of the microalgal biomass. Natural biopolymers, such as chitosan and poly-γ glutamic acid, are safer than metal salts; however, these biopolymers are generally expensive.[9] Cationic polyacrylamides (CPAMs), one of the most commonly used organic polymers, are widely used as

Received: July 24, 2013
Accepted: December 16, 2013
Published: December 16, 2013

flocculants in wastewater treatment and as retention aids in paper making.[10,11] They are characterized by their linear high molecular weight and cationic density. Due to their high flocculation efficiency and low cost, studies on their synthesis, modification, and applications have attracted widespread attention. However, the most commonly used CPAM often contains traces of toxic acrylamide, and acrylamide residue in the final solution limits its applications.[12] In addition, the sedimentation of the flocculated material is generally a time-consuming process. Development of a safe and effective flocculant is necessary for the industrial-scale production of microalgal fuels.

Magnetic flocculation is an emerging technology for microalgae harvesting.[9] The process is based on tagging the target cells with magnetic particles and separating them from the medium by the intrinsic paramagnetic moment in response to an external magnetic field.[13] Magnetic separation has several advantages, such as it is quick, simple, energy-efficient, and inexpensive.[14] Magnetic flocculation has been successfully used for the removal of microalgae from lakes for nearly forty years.[15] Recently, several functionalized magnetic particles, such as surface functionalized magnetic iron oxide nanoparticles with cationic polyelectrolyte poly(diallyldimethylammonium chloride) (PDDA), and magnetic coagulant synthesized by compounding acid-modified fly ash with magnetic Fe_3O_4, have been utilized for algae removal from a fish pond or fresh water, and they resulted in a rapid and effective separation process in both cases.[16,17] In addition, naked Fe_3O_4 nanoparticles, as well as functionalized magnetic particles, have been used for the flocculation of both freshwater and marine microalgae.[18−22] However, the dosage of magnetic particles required for microalgae recovery is still high and may increase the cost of the harvesting step.

The goal of this study is to develop an effective magnetic flocculant for the recovery of *B. braunii* and *C. ellipsoidea*. The synthesis methods of the magnetic flocculant and the operating parameters for the magnetic separation were investigated, and the mechanism of microalgae harvesting by magnetic flocculation is discussed.

2. EXPERIMENTAL SECTION

Algal Strains and Cultivation Conditions. *Botryococcus braunii* and *Chlorella ellipsoidea*, stored in the Institute of Process Engineering, Chinese Academy of Sciences, were cultivated in modified Chu 13 medium and BG 11 medium, respectively. The cultures were cultivated in 250 mL flasks containing 100 mL medium on a rotary shaker at 100 rpm, 25 ± 1 °C. Algal cells were cultured photoautotrophically under a light/dark cycle of 16/8 h with 35 $\mu mol \cdot m^{-2} \cdot s^{-1}$. The initial biomass concentration of *B. braunii* was 0.2 g dry cell weight/L (g DCW/L), and a final concentration of 1.8 g DCW/L was achieved after four weeks. *C. ellipsoidea* grew from an initial concentration of 0.1 g DCW/L to 0.7 g DCW/L after two weeks. The algal broths were directly applied in the separation experiments.

Preparation of the Magnetic Flocculant. Magnetic Fe_3O_4 nanoparticles were synthesized using chemical precipitation.[23] Degassed Millipore water (100 mL) was vigorously stirred under a N_2 atmosphere. As the water was heated to 80 °C, 0.99 g $FeCl_2 \cdot 4H_2O$, and 2.7 g $FeCl_3 \cdot 6H_2O$ were added. Once the salts were completely dissolved, 10 mL NH_4OH (25 wt %) was added and the reaction was kept at 80 °C under constant stirring under a N_2 atmosphere for 30 min. The resulting Fe_3O_4 nanoparticles were collected using a permanent magnet, washed four times with Millipore water, and dispersed in Millipore water for further use.

Cationic polyacrylamide (CPAM), as shown in Figure 1, with a molecular weight of 8×10^6 $g \cdot mol^{-1}$ and a charge density of

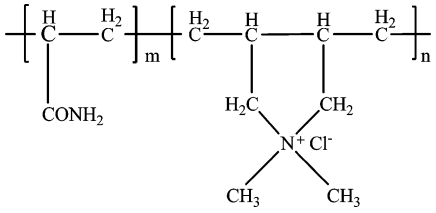


Figure 1. Structure of cationic polyacrylamide (CPAM).

30%, was purchased from Walter Liyuan Environmental Protection Technology Co., Ltd (Beijing, China). The cationic monomer of CPAM is dimethyl diallyl ammonium chloride (DMDAAC). The CPAM was dissolved in degassed Millipore water on a rotary shaker at 150 rpm, 25 °C, and up to 1 mg/mL of magnetic nanoparticles (Fe_3O_4) were gradually added. The resulting magnetic flocculant was collected using a permanent magnet, washed with Millipore water, and dispersed in Millipore water for further use. The synthesis conditions were optimized at various CPAM concentrations and reaction times based on the recovery efficiencies for both *B. braunii* and *C. ellipsoidea*.

Magnetic Separation Procedures. The magnetic flocculant was added to the microalgae broth in Erlenmeyer flasks (1.5 cm depth) and mixed on a rotary shaker at 150 rpm, 25 °C for specific times. The algal−flocculant flocs were concentrated and separated from the suspension medium using a cubic permanent $Nd_2Fe_{14}B$ magnet (5 cm L × 5 cm W × 1 cm H) with a magnetic induction intensity of 2000 G (Hiway electrical Co., Ltd.), which was placed at the bottom of the vessel for 2 min. The magnetic separation conditions were investigated by varying several parameters, including the adsorption times, the pH of the microalgae broth, the flocculant dosage, and the adsorption isotherm. To test the effect of the pH of the microalgae broth on the recovery efficiency, the pH was adjusted in the range 4−10, using either 1 M HCl or 1 M NaOH. To determine the adsorption isotherm, the microalgae were concentrated or diluted to a specific concentration. All experiments were carried out at 25 °C.

To compare the flocculation efficiency of CPAM with the magnetic flocculant, 25 mg/L and 120 mg/L CPAM were added to 20 mL of microalgae broth (pH 7.0) in a 50 mL beaker containing *B. braunii* or *C. ellipsoidea*, respectively. The solution was mixed for 10 min at 150 rpm and then stirred for 2 min at 40 rpm. After sedimentation for 30 minutes, 2 mL of the supernatant was withdrawn using a pipette at 1 cm below the surface to measure the turbidity. All experiments were carried out at 25 °C.

Analytical Methods. To determine the relationship between the optical density at 680 nm (OD_{680}) and the dry biomass, the microalgae culture was diluted or concentrated to a certain OD_{680} value using a UV-2100 spectrophotometer (Unico, Shanghai, China), and then centrifuged for 5 min at 10 000 rpm, at 4 °C. The collected algal pellets were washed three times with distilled water and dried at 105 °C for 24 h to a constant weight. The dry weight (g/L) of the algal biomass was determined gravimetrically.[24]

The recovery efficiency (RE) is defined as the percentage of the dry biomass of the separated algal cells divided by the total dry biomass of the algal cells.

$$\mathrm{RE}(\%) = (1 - M_t/M_0) \times 100\% \quad (1)$$

where M_t is microalgae concentration (biomass, g/L) in the broth after separation and M_0 is the initial microalgae concentration (biomass, g/L) in the culture broth.

The pH value of the culture broth was measured using a digital pH meter. The zeta (ζ) potential was measured using a DelsaNano C Particle Size and Zeta Potential Analyzer (Beckman Coulter Inc.). Pictures of the algal cells and flocs were taken using a light microscope (Leica Microsystems CMS GmbH, Germany). The magnetization hysteresis loop of the naked Fe_3O_4 and CPAM-modified Fe_3O_4 particles were measured using a Vibrating Sample Magnetometer (VSM, Model 7307, Lakeshore, U.S.A.).

The adsorption isotherm represents the equilibrium relationship between the amount of adsorption of the adsorbate and its equilibrium concentration in solution at a certain temperature. It indicates the adsorption capacity of a flocculant and helps to elucidate the adsorption mechanism.[25] The Langmuir and Freundlich models are frequently used to study adsorption isotherms.[26,27] The Langmuir equation is used to describe a monolayer adsorption, whereas the Freundlich model is valid for heterogeneous surfaces possessing different sorption energy sites and can be used to describe either a monolayer or a multilayer adsorption. The linear forms of the Langmuir and Freundlich isotherm models can be expressed by eqs 2 and 3, respectively.

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (2)$$

$$\lg Q_e = \lg K_F + \frac{1}{n} \lg C_e \quad (3)$$

where C_e (g/L) is the equilibrium algal concentration in solution, Q_e (mg/mg-particles) is the amount of microalgae adsorbed onto the magnetic flocculant, Q_m (mg/mg-particles) is the maximum adsorption capacity for monolayer coverage, K_L (L/g) is the Langmuir constant related to the energy of adsorption which increases as the strength of the adsorption bond increases, K_F (mg/mg-particles) and $1/n$ are Freundlich constants related to the adsorption capacity and the heterogeneous sorption sites or adsorption intensity, respectively.

To estimate the fit of the isotherm to the experimental data, the degree of difference (χ^2) obtained by χ-square analysis, and the normalized standard deviation (NSD (%)) was calculated using the following equations:[28]

$$\chi^2 = \sum [(q_e^{\mathrm{exp}} - q_e^{\mathrm{cal}})^2 / q_e^{\mathrm{cal}}] \quad (4)$$

$$\mathrm{NSD}(\%) = 100 \times \sqrt{\{\sum [(q_e^{\mathrm{exp}} - q_e^{\mathrm{cal}})/q_e^{\mathrm{exp}}]^2\}/(N-1)} \quad (5)$$

where q_e^{cal} (mg/mg-particles) is the equilibrium adsorption capacity calculated from the isotherm model and q_e^{exp} (mg/mg-particles) is the experimental equilibrium capacity obtained from the experimental data. N is the number of experimental trials. Smaller χ^2 and NSD values indicate a better fit of the isotherm model.

3. RESULTS AND DISCUSSION

3.1. Synthesis of the Magnetic Flocculant. The magnetic flocculant was synthesized to test its effectiveness for harvesting *B. braunii* and *C. ellipsoidea* cells. As shown in Figure 2, the saturation magnetization of the magnetic flocculant was 68.413 emu/g, which was similar with the naked Fe_3O_4 particles. Accompanied by a coercivity of 2.305 G, the magnetic flocculant shows superparamagnetic properties with a high saturation magnetization, which indicates it could be easily separated from the solution by an external magnetic field. As described in the Supporting Information (Figure S1), the recovery efficiencies for both algal species improved as the reaction time between the Fe_3O_4 nanoparticles and the CPAM increased, and the maximum recovery efficiencies were obtained at a reaction time of 15 min. The recovery efficiencies

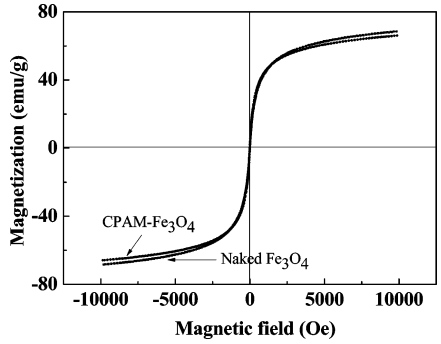


Figure 2. Magnetization hysteresis loop of naked Fe_3O_4 and CPAM modified Fe_3O_4.

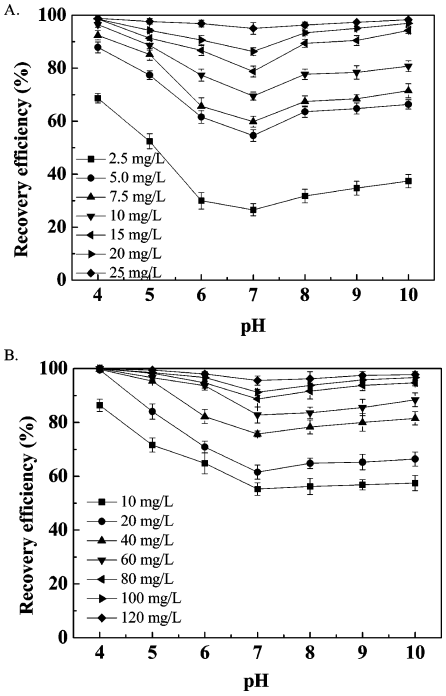


Figure 3. Effect of the pH value and particle dosage on the recovery efficiencies of *B. braunii* (A) and *C. ellipsoidea* (B). The reaction time of the particles and microalgae was 10 min.

dx.doi.org/10.1021/am404764n | ACS Appl. Mater. Interfaces 2014, 6, 109−115

Table 1. Comparison of Various Magnetic Materials on Microalgal Harvesting

microalgae species	initial algal concentration (g/L)	reagents	dosage (mg/L)	recovery efficiency	adsorption capacity (mg/mg-particles)	process time (min)	refs
B. braunii	1.8	naked Fe_3O_4 particles	75	~98% pH 7	55.9	3	18
B. braunii	1.8	CPAM-Fe_3O_4 magnetic flocculant	25	95% pH 7	114.8	⩽10	this study
C. ellipsoidea	0.8	naked Fe_3O_4 particles	300	> 98% pH 7	5.83	3	18
C. vulgaris	1.3	silica-coated magnetic particles	1300	> 90% pH 9−12	4.6	6−15	19
Chlorella sp	not mentioned	PDDA-rodlike Fe_3O_4 nanoparticles	200	99%	not mentioned	>15	20
C. vulgaris	0.3	naked Fe_3O_4 particles	240	<20% pH 7	not mentioned	11−12	22
C. ellipsoidea	0.7	CPAM-Fe_3O_4 magnetic flocculant	120	96% pH 7	21.4	⩽10	this study

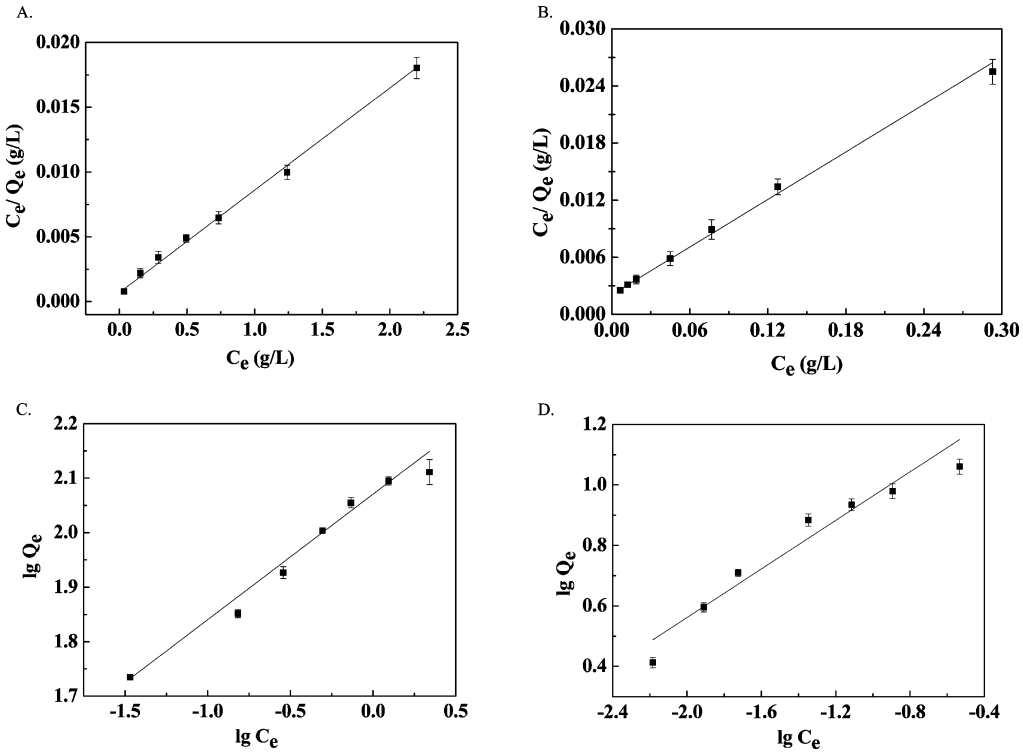


Figure 4. Adsorption isotherms of *B. braunii* (A, C) and *C. ellipsoidea* (B, D) cells on magnetic particles fit to the Langmuir model and the Freundlich model. (A and B) Lagnmuir model; (C and D) Freundlich model. Particle dosage: 25 mg/L for *B. braunii* and 120 mg/L for *C. ellipsoidea*. Reaction time of particles and microalgae: 10 min. pH of microalgae broth: 7.0. 25 °C.

Table 2. Estimated Parameters from the Langmuir and Freundlich Models at 25 °C and pH = 7.0[a]

	Langmuir model						Freundlich model					
microalgae	Q_m (mg/mg-particles)	K_L (L/g)	R^2	χ^{2b}	p^c	NSD (%)	K_F (mg/mg-particles)	$1/n$	R^2	χ^{2b}	p^c	NSD (%)
B. braunii	135.5 ± 13.2	8.11 ± 0.92	0.996	7.11	0.029	74.4	114.8 ± 4.3	0.233 ± 0.04	0.966	1.69	0.383	26.8
C. ellipsoidea	12.4 ± 2.6	34.37 ± 2.24	0.997	9.23	0.011	57.9	21.4 ± 1.5	0.385 ± 0.11	0.932	2.07	0.320	19.7

[a]Data are represented as the mean ± standard deviation of triplicates. [b]The degrees of freedom (v) in the χ^2 tests are 2. [c]p is the probability of Type I error when fitting model to data.

of both *B. braunii* and *C. ellipsoidea* were drastically improved when the concentration of CPAM was increased from 0 to 0.1 mg/mL (Supporting Information, Figure S2). Increasing the CPAM concentration above 0.1 mg/mL did not further improve the harvesting efficiencies because the Fe_3O_4 particles were saturated with CPAM at that point.

3.2. Magnetic Separation of Microalgae. The recovery efficiencies for both species slowly increased from 2 to 10 minutes to the maximum value (Supporting Information, Figure S3). As shown in Figure 3, the pH of the culture broth is an important factor in the magnetic separation process. A low pH value was favorable for the recovery of both *B. braunii* and *C. ellipsoidea* cells, and the recovery efficiencies for both species decreased as the pH increased up to pH 7. An increase above 7 led to a slight increase in the recovery efficiencies for both species. In addition, an increase in particle dosage increased the recovery of both species at all pH values tested. The recovery efficiencies were higher than 95% at a flocculant dosage of 25

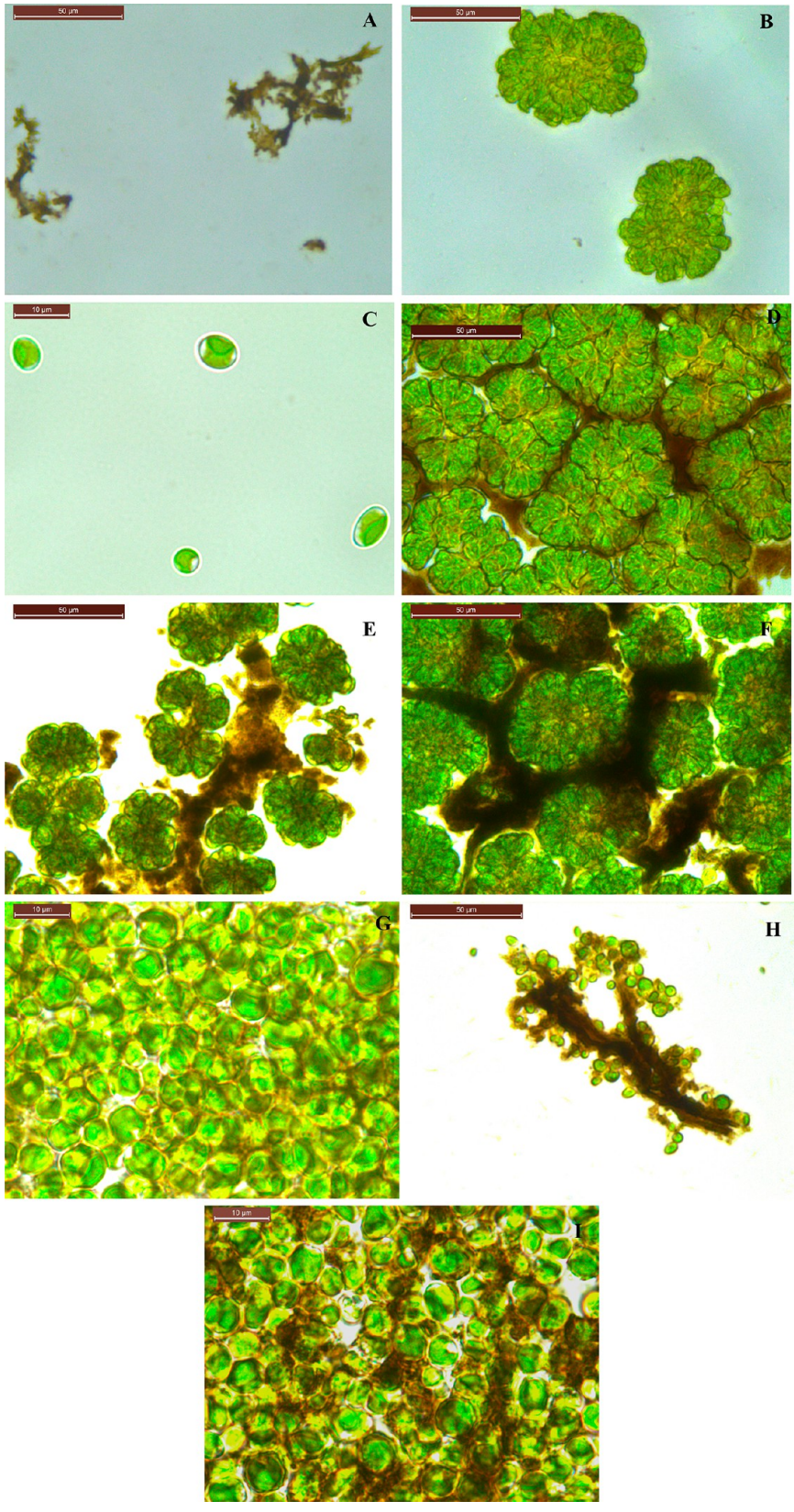


Figure 5. Light microscope photos of free particles (A), free microalgal cells (B, C), naked Fe_3O_4-cell aggregates following concentration with a permanent magnetic (D, G), CPAM-Fe_3O_4-cell aggregates prior to concentration with a permanent magnetic (E, H), and CPAM-Fe_3O_4-cell aggregates after concentration with a permanent magnetic (F, I). (A) ×400; (B, D, E, and F) *B. braunii* (×400); (C, G, and I) *C. ellipsoidea* (×1000); (H) *C. ellipsoidea* (×400).

mg/L for *B. braunii* and at a flocculant dosage of 120 mg/L for *C. ellipsoidea*. The higher flocculant dosage required for the recovery of *C. ellipsoidea* compared to *B. braunii* was consistent with results reported by Xu et al.[18] This is primarily due to the

dx.doi.org/10.1021/am404764n | *ACS Appl. Mater. Interfaces* 2014, 6, 109−115

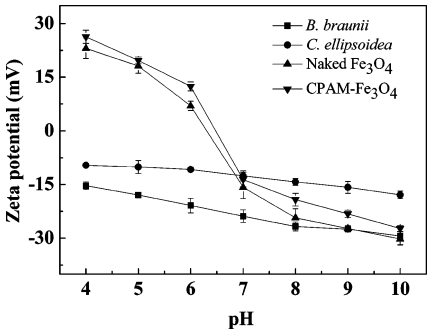


Figure 6. ζ-potential of the microalgae and magnetic flocculant at different pH values.

smaller cell size of *C. ellipsoidea*. This results in a higher specific surface area and, therefore, requires more flocculant to achieve a similar recovery efficiency as for *B. braunii*.[18]

In comparison with other magnetic reagents,[18−20,22] the magnetic flocculant in this study resulted in a similar harvesting efficiency using a low flocculant dosage (Table 1). Compared with CPAM, the magnetic flocculant was more rapid and effective. Using an equal amount of the magnetic flocculant and CPAM, the microalgal cells aggregated into large flocs. However, the flocs produced by the magnetic flocculant were quickly and effectively sedimented within 60 s using a permanent magnet, while the flocs that resulted from the use of CPAM remained suspended in solution and required a much longer time period for sedimentation (Supporting Information, Figure S4). The flocculation efficiency using CPAM only reached 57.33% and 84.45% for *B. braunii* and *C. ellipsoidea* after sedimentation for 30 min, respectively. No magnetic flocculant was detected in the supernatant after the magnetic separation (data not shown). For the application of magnetic algal harvesting in the large-scale culture system (e.g. raceway pond), a set of separation system including mixing tank and magnetic separator have been designed and will be investigated in the further study.

3.3. Adsorption Isotherm. The fit of the adsorption isotherms of *B. braunii* and *C. ellipsoidea* cells with the magnetic flocculant with the Langmuir model and the Freundlich model are shown in Figure 4. The values of Q_m and K_L were calculated from the slope and intercept of the linear plots of C_e/Q_e versus C_e from eq 2, and the values of K_F and $1/n$ were obtained from eq 3, along with their correlation factors (R^2). The χ^2 and NSD values are summarized in Table 2. Although the correlation factors (R^2) of both the Langmuir and Freundlich isotherms were high ($R^2 > 0.93$), the χ^2 and NSD values of the Freundlich model were much smaller than those of the Langmuir model. This indicates that the Freundlich isotherm was a better model than the Langmuir isotherm and indicates that the flocculation process in this study was multilayer adsorption onto heterogeneous sites. The heterogeneous multilayer coverage of the microalgal cells by the magnetic particles was also observed using light microscopy (Figure 5 E, H). The adsorption capacity, described by the K_L of the particles, was higher for *B. braunii* than for *C. ellipsoidea* at the tested temperature. This is because the smaller size of the *C. ellipsoidea* cells result in a larger specific surface area and require more magnetic flocculant in comparison with the larger *B. braunii* cells.[18] The maximal adsorption capacity from the Freundlich model was calculated as 114.8 mg/mg-particles and 21.4 mg/mg-particles for *B. braunii* and *C. ellipsoidea*, respectively. In addition, the $1/n$ values from the Freundlich model indicate that the adsorption process was straightforward because the values were below 1 for both microalgal strains at the temperature tested.[29] A similar adsorption capacity was obtained from the Q_m values in the Langmuir model. The K_L values in this study were higher than those in the naked Fe_3O_4 nanoparticles adsorption process, which indicates that the algal cells bonded the magnetic flocculant more tightly than the naked particles. In addition, *C. ellipsoidea* cells bonded to the flocculant more tightly than *B. braunii* cells.[18]

3.4. Possible Separation Mechanism of the Magnetic Flocculant. In general, the flocculation process is a result of four basic mechanisms: charge neutralization, double layer compression, sweep flocculation, and bridging.[30] The ζ-potential measurement showed that both *B. braunii* and *C. ellipsoidea* cells were negatively charged at the tested pH values (ranging from 4 to 10). The ζ-potential of the magnetic flocculant exhibited a positive charge when the pH value was below 7.0 and a negative charge when the pH was above 7.0 (Fig. 6). Charge neutralization and double layer compression occur when the two particles have an opposite charge. In this process, both the magnetic flocculant and the algal cells were negatively charged when the pH value was above 7.0; therefore, charge neutralization and double layer compression are unlikely to be the main mechanisms in this flocculation process. In addition, charge neutralization only acts as an auxiliary interaction force in acidic conditions. Sweep flocculation is based on the formation of metal hydroxide. It was also not a possible primary mechanism in this study because it is not functional at acidic or neutral conditions, and there were trace metal ions in the final microalgae broth.[31] Therefore, the predominant mechanism in this flocculation process was bridging. The observations using microscopy indicated that the microalgal cells were adsorbed onto the surface of the magnetic flocculant and that they were bridged into large flocs (Figure 5E, F, H, I). It has been reported (in the flocculation of kaolin) that, at low concentrations, CPAM causes flocculation by bridging, while at high concentrations the main mechanism becomes charge neutralization.[11] In acidic or alkali solutions, large chain deformation occurs, which improves the interaction between the CPAM and the suspended particles.[32] This mechanism resulted in an increase in the flocculation efficiency in alkali conditions (Figure 3).

4. CONCLUSION

A magnetic flocculant synthesized using magnetic Fe_3O_4 particles and CPAM was developed for efficient microalgal harvesting. A harvesting efficiency of over 95% was obtained at a dosage of 25 mg/L for *B. braunii* and 120 mg/L for *C. ellipsoidea* within 10 min. The adsorption mechanism was determined to be primarily a result of the electrostatic attraction and bridging between the magnetic flocculant and the microalgal cells. The magnetic flocculant was more rapid and efficient compared to a traditional flocculant, such as CPAM, and did not result in flocculant contamination in the solution. In addition, an equal harvesting efficiency with other magnetic reagents can be obtained using a low flocculant dosage. The magnetic flocculant synthesized in this study offers the potential for an efficient and rapid method for algal harvesting that does not result in environmental pollution.

■ ASSOCIATED CONTENT

Supporting Information

Effect of magnetic flocculant synthesis conditions on microalgal recovery efficiency, the effect of the adsorption time of the flocculant and microalgae on microalgal recovery efficiency, and the images of the microalgal flocculation process. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*Tel/Fax: +86-10-82622280. E-mail: czliu@home.ipe.ac.cn.
*E-mail: cguo@home.ipe.ac.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by the Major State Basic Research Development Program (973 Project) of China (Nos. 2011CB200905 and 2011CB200903), the National Natural Science Foundation of China (No. 21106165), and the Chinese Academy of Sciences Fellowship for Young International Scientists (No. 2011Y1GA01).

■ REFERENCES

(1) Chisti, Y. *Biotechnol. Adv.* **2007**, *25*, 294−306.
(2) Mata, T.M.; Martins, A.A.; Caetano, N.S. *Renewable Sustainable Energy Rev.* **2010**, *14*, 217−232.
(3) Casadevall, E.; Dif, D.; Largeau, C.; Gudin, C.; Chaumont, D.; Desanti, O. *Biotechnol. Bioeng.* **1985**, *27*, 286−295.
(4) Danquah, M.K.; Gladman, B.; Moheimani, N.; Forde, G.M. *Chem. Eng. J.* **2009**, *151*, 73−78.
(5) Tenney, M.W.; Echelberger, W.F.; Schuessler, R.G.; Pavoni, J.L. *Appl. Microbiol.* **1969**, *18*, 965−971.
(6) Stephens, E.; Ross, I.L.; King, Z.; Mussgnug, J.H.; Kruse, O.; Posten, C.; Borowitzka, M.A.; Hankamer, B. *Nat. Biotechnol.* **2010**, *28*, 126−128.
(7) Williams, P.J.L.; Laurens, L.M.L. *Energy Environ. Sci.* **2010**, *3*, 554−590.
(8) Uduman, N.; Qi, Y.; Danquah, M.K.; Forde, G.M.; Hoadley, A. *J. Renewable Sustainable Energy* **2010**, *2*, 012701.
(9) Vandamme, D.; Foubert, I.; Muylaert, K. *Trends Biotechnol.* **2013**, *31*, 233−239.
(10) Bolto, B.A. *Prog. Polym. Sci.* **1995**, *20*, 987−1041.
(11) McCarron, A.M.; Crispo, S.; Smith-Palmer, T. *J. Appl. Polym. Sci.* **2002**, *83*, 2382−2389.
(12) Bolto, B.; Gregory. *J. Water Res.* **2007**, *41*, 2301−2324.
(13) Chalmers, J.J.; Zborowski, M.; Moore, L.; Mandal, S.; Fang, B.B.; Sun, L.P. *Biotechnol. Bioeng.* **1998**, *59*, 10−20.
(14) Yavuz, C.T.; Prakash, A.; Mayo, J.T.; Colvin, V.L. *Chem. Eng. Sci.* **2009**, *64*, 2510−2521.
(15) Bitton, G.; Fox, J.L.; Strickland, H.G. *Appl. Microbiol.* **1975**, *30*, 905−908.
(16) Toh, P.Y.; Yeap, S.P.; Kong, L.P.; Ng, B.W.; Chan, D.J.C.; Ahmad, A.L.; Lim, J.K. *Chem. Eng. J.* **2012**, *211*, 22−30.
(17) Liu, D.; Wang, P.; Wei, G.R.; Dong, W.B.; Hui, F. *Environ. Sci. Pollut. Res.* **2013**, *20*, 60−65.
(18) Xu, L.; Guo, C.; Wang, F.; Zheng, S.; Liu, C.Z. *Bioresour. Technol.* **2011**, *102*, 10047−10051.
(19) Cerff, M.; Morweiser, M.; Dillschneider, R.; Michel, A.; Menzel, K.; Posten, C. *Bioresour. Technol.* **2012**, *118*, 289−295.
(20) Lim, J.K.; Chieh, D.C.J.; Jalak, S.A.; Toh, P.Y.; Yasin, N.H.M.; Ng, B.W.; Ahmad, A.L. *Small* **2012**, *8*, 1683−1692.
(21) Hu, Y.R.; Wang, F.; Wang, S.K.; Liu, C.Z.; Guo, C. *Bioresour. Technol.* **2013**, *138*, 387−390.
(22) Prochazkova, G.; Safarik, I.; Branyik, T. *Bioresour. Technol.* **2013**, *130*, 472−477.
(23) Kang, Y.S.; Risbud, S.; Rabolt, J.F.; Stroeve, P. *Chem. Mater.* **1996**, *8*, 2209−2211.
(24) Pruvost, J.; Van Vooren, G.; Cogne, G.; Legrand, J. *Bioresour. Technol.* **2009**, *100*, 5988−5995.
(25) Chang, Y.P.; Ren, C.L.; Qu, J.C.; Chen, X.G. *Appl. Surf. Sci.* **2012**, *261*, 504−509.
(26) Langmuir, I. *J. Am. Chem. Soc.* **1918**, *40*, 1361−1403.
(27) Freundlich, H.M.F. *Ind. Eng. Chem. Fundam.* **1906**, *57*, 387−470.
(28) Ding, D.H.; Zhao, Y.X.; Yang, S.J.; Shi, W.S.; Zhang, Z.Y.; Lei, Z.F.; Yang, Y.N. *Water Res.* **2013**, *47*, 2563−2571.
(29) Wu, J.; Yu, H.Q. *Bioresour. Technol.* **2007**, *98*, 253−259.
(30) Miller, S.M.; Fugate, E.J.; Craver, V.O.; Smith, J.A.; Zimmerman, J.B. *Environ. Sci. Technol.* **2008**, *42*, 4274−4279.
(31) Ghernaouta, D.; Ghernaout, B. *Desalin. Water Treat.* **2012**, *44*, 15−28.
(32) Gui, Z.L.; Qian, J.W.; Li, X.K.; Zheng, B.Q.; An, Q.F. *J. Appl. Polym. Sci.* **2010**, *117*, 2915−2922.