

Article

Fabrication of Magnetic Silica Nanomaterials and Their Effects on Algal Harvesting

Yuewen Zhang ^{1,2}, Peirui Liu ^{1,2} and Yu Hong ^{1,2,*}

¹ Beijing Key Lab for Source Control Technology of Water Pollution, College of Environmental Science and Engineering, Beijing Forestry University, Beijing 100083, China

² Engineering Research Center for Water Pollution Source Control & Eco-Remediation, College of Environmental Science and Engineering, Beijing Forestry University, Beijing 100083, China

* Correspondence: yuhong829908@gmail.com

Abstract: Harmful algal blooms are a global problem in water environments, and their explosive growth endangers the health of aquatic ecosystems. Magnetic nanomaterials for the harvesting of microalgae have received a lot of attention because of their high efficiency, low cost, and ease of operation. In this study, magnetic mesoporous silica nanomaterials were prepared using Fe₃O₄ as a carrier and harvesting on *Chlorella* sp. HQ. It was found that silica coated with magnetic Fe₃O₄ microspheres has good dispersion. The harvesting of *Chlorella* sp. HQ via magnetic mesoporous silica could be maintained over a wide pH range (4 to 12). After the removal of organic components from the surface of the material, the magnetic mesoporous silica obtained a better porous structure. The ethanol reflux method was more beneficial than the calcination method in maintaining the stable structure of the material, thus improving the harvesting efficiency of the material for the microalgae *Chlorella* sp. HQ by a maximum of 17.8% (65.9% to 83.7%). When the molar ratio of active agent cetyltrimethylammonium bromide (CTAB) and stabilizer polyvinylpyrrolidone (PVP) was 1: 0.092 at pH 4 and algal concentration of 0.5 g/L, the materials showed the maximum harvesting efficiency of *Chlorella* sp. HQ was 84.2%.

Keywords: Fe₃O₄; magnetic mesoporous silicon; microalgae harvesting; *Chlorella* sp. HQ



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1. Introduction

Water environment problems are becoming more and more prominent worldwide, and water shortages and the serious pollution of water bodies have received strong attention from the international community [1]. With the rapid development of agriculture and industry, the large amounts of nitrogen and phosphorus discharged into the water environment have made the eutrophication of water bodies more and more serious, and eutrophication has led to the explosive growth of water blooms, causing an ecological crisis. The control of water blooms has been a hot spot of research in recent years [2]. At present, the main domestic and international techniques for controlling water blooms include chemical and mechanical removal, nutrient control, aeration and mixing, hydrodynamic control, and biological control [3]. In addition to the pollution of water bodies, chemical methods may also have toxic effects on other biological species such as fish; the cost and energy consumption of mechanical removal methods are too high; nutrient control methods are too expensive; the energy consumption and operating costs of aeration mixing methods are too high; the energy consumption of hydrodynamic control methods is too high; and biological removal methods are time-consuming and the removal effect is not satisfactory.

Microalgae are a double-edged sword, with explosive growth of algae endangering the health of water ecosystems [4]. On the other hand, the microalgae culture process can use nutrients such as nitrogen and phosphorus in water, and the use of microalgae to purify water bodies has received much attention in recent years [5]. Whether it is the removal of

harmful algae or the purification of water bodies using beneficial algae, the efficient harvesting of microalgae is of great research importance [6]. However, due to the small cell size and high water content of microalgae, traditional microalgae harvesting techniques are still dominated by power centrifugation, filtration, flotation, and sedimentation [7]. However, these commonly used traditional microalgae harvesting methods all have economic and technical drawbacks [8], such as high costs, high energy use, complex operation methods, imperfect technology, and low harvesting efficiency, which have limited their applications. Nanomaterials possess high specific surface areas and excellent adsorption properties and have great application prospects in environmental remediation, catalysis, and adsorption. Magnetic nanomaterials not only have the properties of nanoparticles, but are also highly regarded for their unique magnetic properties. Using magnetic separation to avoid secondary pollution of water bodies, the separated magnetic nanomaterials can be regenerated and recycled, thus saving costs [9–11]. Harvesting microalgae using magnetic nanomaterials is simpler and more efficient than traditional methods and has good prospects for application. Currently, the magnetic harvesting of microalgae mainly involves the use of Fe_3O_4 or its modifiers to collect the material contained in the liquid suspension of microalgae under the action of an external magnetic field, which has a significant effect on reducing the energy consumption of microalgae [12]. It was found that the harvesting efficiency of microalgae could reach more than 95% within 2 min [13]. However, due to the dissolution of Fe cations on the surface of Fe_3O_4 , large amounts of metal cations are produced locally, which are toxic to the organisms [14]. Studies have shown that coating the surface of Fe_3O_4 nanoparticles with noble metals, metal oxides, and inorganic silica can effectively mitigate their toxic effects [15]. Liu et al. [16] prepared magnetic graphene oxide that achieved 95.35% microalgae harvesting efficiency within 5 min. Subsequently, they prepared PA-modified porous Fe_3O_4 microspheres (p- Fe_3O_4 @PA) using long-chain polyarginine (PA), which provided a rich adsorption medium and active sites for *Chlorella vulgaris*, and p- Fe_3O_4 @PA significantly improved the harvesting efficiency of *C. vulgaris* [17]. Gerulová et al. [18] investigated the effect of magnetic Fe_3O_4 -polyethyleneimine nanomaterials on the harvesting of several green algae. It was found that the magnetic material achieved 95%, 97%, 90%, and 97% harvesting efficiency for *Chlorella zofingiensis*, *C. vulgaris*, *Chlorella sorokiniana*, and *Chlorella ellipsoidea*, respectively. They also compared the differences in magnetic harvesting of Fe_3O_4 -PEI nanocomposites on two species of green algae and *Microcystis aeruginosa*. It was found that the magnetic harvesting materials had adsorption effects on different algal species, and the materials did not differ much on *C. vulgaris*, *Auxenochlorella protothecoides*, and *Microcystis aeruginosa*, with the adsorption amounts of 4.932, 4.735, and 4.871 g/g, respectively [19]. In summary, finding a good biocompatible and cost-effective magnetic capture material is a key to this study.

Amongst many materials, mesoporous silica materials have excellent properties, with high specific surface areas and ordered and tunable pore channels, and they are widely studied and used in multidisciplinary fields [20]. The large number of hydroxyl groups on the surface of silicon dioxide, its low isoelectric point, and its water-repellent properties allow it to be used as a superabsorbent. The magnetic material can be compounded with mesoporous silica to obtain magnetic mesoporous silica composite particles. In previous studies, several magnetic silica composite nanomaterials have been synthesized and have shown good adsorption properties for both heavy metals and organic pollutants [21,22]. However, magnetic mesoporous silica materials are currently used in wastewater treatment and have fewer applications in microalgae separation [23]. Understanding and studying the properties, electrical properties, and surface functional groups of algal cells fundamentally determines the design of algal harvesting materials [24]. The main functional groups on the surface of microalgae are carboxyl, phosphate, and amine or hydroxyl groups, and algal cells have a negative ζ -potential in the culture medium [25]. This may explain the limited use of magnetic silica in capturing isolated microalgae, as they carry the same type of charge. Therefore, it is important to study the harvesting of microalgae using magnetic silica.

In this work, we prepared magnetic silica materials and modified them to prepare magnetic mesoporous materials. Firstly, Fe_3O_4 magnetic particles were used as carriers, and SiO_2 was used to surface coat them, thus obtaining composite particles. This composite particle effectively solves the recycling problem of the adsorbent, greatly improves the efficiency of the adsorption and separation process, reduces the operation cost, and at the same time reduces the secondary pollution to the environment. This paper studies the removal and harvesting effect of this composite material on microalgae *Chlorella* sp. HQ to provide theoretical support for the harvesting of microalgae in the real environment.

2. Materials and Methods

2.1. Microalgal Cultivation

The algal species selected for this paper is *Chlorella* sp. HQ (No. GCMCC7601), preserved in the Chinese Centre for Microbial Culture, which was isolated in a previous study [26]. *Chlorella* sp. HQ has good robustness and growth potential under different cultural conditions [27,28]. *Chlorella* sp. HQ was cultured in 500 mL conical flasks with 300 mL of medium to ensure an initial algal density of 2×10^5 cells/mL and placed in an artificial incubator (HPG-280H, HDL, China) at 25 °C. The optical density of the incubator was set at 60 $\mu\text{mol}/\text{m}^2 \text{ s}$, and the light/dark ratio was 14:10 [29]. The medium used for the *Chlorella* headquarters is SE medium, which has the following composition: 250.000 mg/L NaNO_3 , 75 mg/L $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$, 75 mg/L $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 25 mg/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 175 mg/L KH_2PO_4 , 25 mg/L NaCl , 5 mg/L $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 81 $\mu\text{g}/\text{L}$ FeCl_3 , 10 mg/L Na_2EDTA , 2860 $\mu\text{g}/\text{L}$ H_3BO_3 , 1810 $\mu\text{g}/\text{L}$ $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, 220 $\mu\text{g}/\text{L}$ $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$, 79 $\mu\text{g}/\text{L}$ $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and 39 $\mu\text{g}/\text{L}$ $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ [26].

2.2. Preparation of Magnetic Folded Mesoporous Silica

2.2.1. Preparation of Magnetic Fe_3O_4

The magnetic Fe_3O_4 nanoparticles were first prepared using a modified chemical coprecipitation method [30]. First, 0.99 g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (>99%) and 2.70 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (>98%) were dissolved in 50 mL deionized water and the suspension was heated to 353 K under nitrogen. Then, 10 mL of NH_4OH (25%) was added dropwise to bring the pH to between 10 and 11, and the mixture was stirred continuously for 30 min. When the color of the solution changed from brown to black, it indicated the formation of Fe_3O_4 . The prepared ferric tetroxide material was magnetically separated and washed several times with deionized water until neutral and set aside.

2.2.2. Preparation of Magnetic Mesoporous Silicon Materials

Pleated magnetic silica nanoparticles (WMSNs) were prepared by improving the method of previous researchers [31]. The mixture was first mixed with 0.5 g of tetraethoxysilane and 4 mL of cyclohexane in a Fe_3O_4 dispersion and sonicated for 10 min at room temperature, with the sonication frequency set to 40 kHz. The mixture was transferred to a mixture of deionized water, ethanol, cetyltrimethylammonium bromide (CTAB), and polyvinylpyrrolidone (PVP) at doses of 25 mL, 15 mL, 0.08 g, and (0–1 g), respectively, at 35 °C with vigorous stirring. The concentration of CTAB was 0.02 mol/L. PVP was set at four different concentrations of 0, 0.005, 0.01, and 0.02 mol/L, and the two were reacted for 1 h. Magnetic mesoporous silica (MSN0, MSN1, MSN2, MSN3) was prepared by setting different CTAB to PVP molar ratios of 1: (0, 0.023, 0.046, 0.092). The silica materials (SN0, SN1, SN2, SN3) could be prepared by this method without the addition of Fe_3O_4 .

During the above preparation, 0.5 mL of NH_4OH was added as a hydrolysis additive to promote the hydrolysis of the tetraethoxysilane. After 4 h, the resulting emulsified solution was transferred to a stainless-steel autoclave lined with PTFE, which was sealed and maintained in an oven at 100 °C for 12 h. The material was then filtered, washed with water, and dried at room temperature for 6 h. Finally, it was calcined and the organic components were removed via calcination at 550 °C for 6 h. At the same time, the organic component of the magnetic material could also be removed via reflux condensation. The

resulting product was dissolved in 2 mL of 1 M HCl, 57.3 mL of ethanol, and 2 mL of deionized and refluxed for 0.5 h at 75 °C, repeated three times. The final magnetic silica materials obtained from the experiment were labeled as WMSN0, WMSN1, WMSN2, and WMSN3.

2.3. Characterization of the Physicochemical Properties of Magnetic Silica

The surface morphology of magnetic silica was observed using Transmission Electron Microscopy (TEM, FEI Tecnai T20, FEI, Portland, OR, USA). Dynamic light scattering (DLS, DynaPro NanoStar, Wyatt, Santa Barbara, CA, USA) was used to study the dynamic behavior of nanoparticles in liquids to obtain information on the hydrodynamic radius and size distribution of magnetic silica nanoparticles. The zeta potential of magnetic silica materials and microalgae was determined using a Malvern laser particle size meter (Zetasizer Nano ZS90, Malvern Instruments, Malvern, UK). The range of motion was ± 10 ucm/Vs, the conductivity range was 0–200 MS/cm, and the temperature range was 2 to 90 °C. The optical density values of OD₆₉₀ for *Chlorella* were measured using a UV-Vis spectrophotometer (UV-2550, Shimadzu, Kyoto, Japan). *Chlorella* cells were washed twice with deionized water and then dried overnight in an oven at 80 °C to obtain the dry cell weight (DCW) [32]. The experiment was repeated three times, and the results obtained are the mean \pm standard deviation of three parallel experiments.

2.4. Harvesting of *Chlorella* using Magnetic Mesoporous Silica

When *Chlorella* sp. HQ reached its maximum biomass in the culture medium, magnetic silica nanomaterials were added to the suspension and the mixture was shaken at 250 rpm for 20 min at 25 °C in a conical flask to carry out the harvesting experiments. The effect of the molar ratio of reactant to stabilizer in the preparation of magnetic silica on the harvesting effect and the effect of the method of removing the active agent from the mesoporous structure on the harvesting effect were investigated separately. At the end of the experiment, the nanomaterial-encapsulated *Chlorella* sp. HQ cells were concentrated and the material–algae floc was separated from the suspension using a magnet outside the vessel conical flask, and the supernatant was left to be tested.

The effect of pH of the *Chlorella* sp. HQ culture solution and the initial concentration of *Chlorella* sp. HQ on magnetic harvesting was also investigated in this study. The pH of the algal culture solution was adjusted to a range of 4–12 using 0.1 M HCl or 0.1 M NaOH, and different types of algal harvesting materials (WMSN0, WMSN1, WMSN2, WMSN3) were added to it to investigate the effect of pH on the harvesting effect [33]. The algal solution concentrations were set at 0.2, 0.5, and 1 g/L; the pH of the algal solution was set at 8; and the rest of the conditions were the same to investigate the effect of the initial concentration of the algal solution on the harvesting effect.

2.5. Data Analysis and Modeling Study

Algal cells coated with magnetic silica nanomaterials are concentrated and separated from the suspension using magnets. After magnetic separation, the density of algal cells in the supernatant was measured. The optical density of the algal cell suspension before and after microalgae harvesting was measured using a UV spectrophotometer at a wavelength of 690 nm to obtain the harvesting efficiency of the algal cells. The initial algal cell density in this study was 0.2 g/L, which is the DCW. The concentration of the algal suspension can be calculated from the linear Equation (1) between the optical density value of the algal solution at 690 nm (OD₆₉₀) and the DCW obtained using the weighing method. The harvesting efficiency of microalgae was calculated from Equation (2) [10].

$$\text{DCW} = 0.151 \times \text{OD}_{690} - 0.00345 \quad (1)$$

$$\text{Magnetic harvesting efficiency of microalgae (\%)} = (C_0 - C_t)/C_0 \times 100 \quad (2)$$

where C_0 and C_t are the biomass concentrations of microalgae (g/L) before and after magnetic harvesting, respectively.

3. Results and Discussion

3.1. Material Characterization Morphology and Structure

The morphology and structure of the silica and magnetic silica nanoparticles are shown in Figures 1 and 2. It can be observed using transmission electron microscopy that the silica nanoparticles are poorly dispersed; they are relatively large in size, about 100–200 nm (Figure 1a–d); and the surface of the nanoparticles is much looser after the removal of the organic layer (Figure 1f). Figure 2 shows that during the formation of magnetic silica nanoparticles, some Fe_3O_4 nanoparticles formed spontaneously and did not show a silica-coated core–shell structure (Figure 2b). Also, it can be seen that the magnetic silica nanoparticles formed a porous hollow structure (Figure 2d is more obvious). After calcination treatment, the porous structure became more evident, and pleated particles were formed (Figure 2f). The silicon dioxide layer was uniformly coated with magnetic Fe_3O_4 microspheres, and the resulting magnetic mesoporous silica microspheres had a good dispersion without agglomeration, with a silicon layer thickness of approximately 50 nm and mesopores with a pore size of approximately 3 nm present in the silicon layer [34].

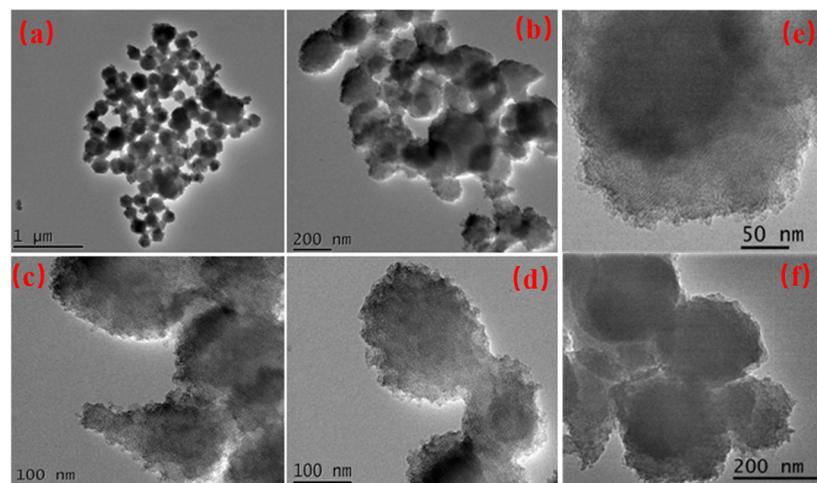


Figure 1. TEM images of silica nanoparticles (a–d) before and (e,f) after the removal of the organic layer.

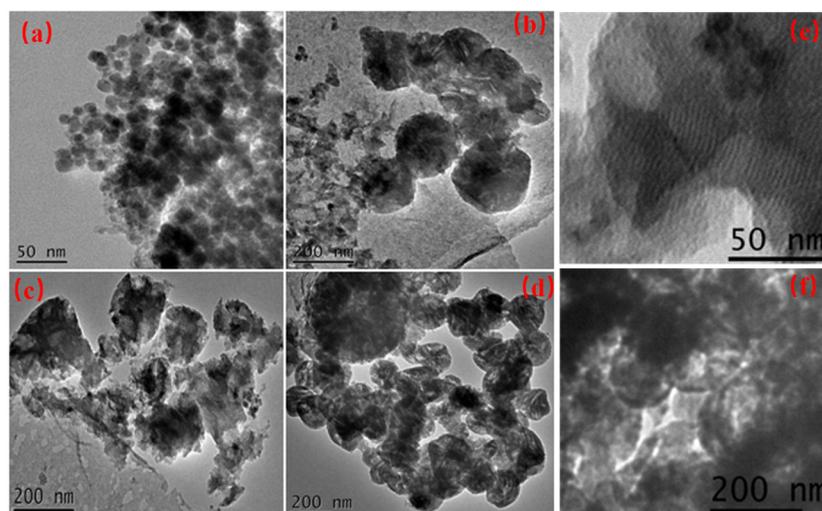


Figure 2. TEM images of magnetic silica nanoparticles (a–d) before and (e,f) after being calcined.

The particle size and distribution of silica and magnetic silica nanoparticles were further compared using DLS. Figure 3a,b correspond to the distribution of the materials before and after the removal of organic components during preparation using the reflux method, respectively. It can be seen that the hydrodynamic sizes of the silica particles are between 300 nm and 1 μm , and the magnetic silica nanoparticles are in two ranges of hydrodynamic sizes, which may come from Fe_3O_4 nanoparticles and uncoated silica nanoparticles, respectively (Figure 3a). The size of the magnetic composite core-shell nanoparticles was larger than the size of the individual magnetic and silica nanoparticles, as they were encapsulated by the silica layer. After the removal of the organic component, the hydrodynamic size of the silica nanoparticles prepared by refluxing increased (Figure 3), while the hydrodynamic size of the magnetic silica nanoparticles prepared by calcination decreased (Figure 2). Therefore, the organic layer on the surface of the material can be removed more completely and form a better porous structure after calcination.

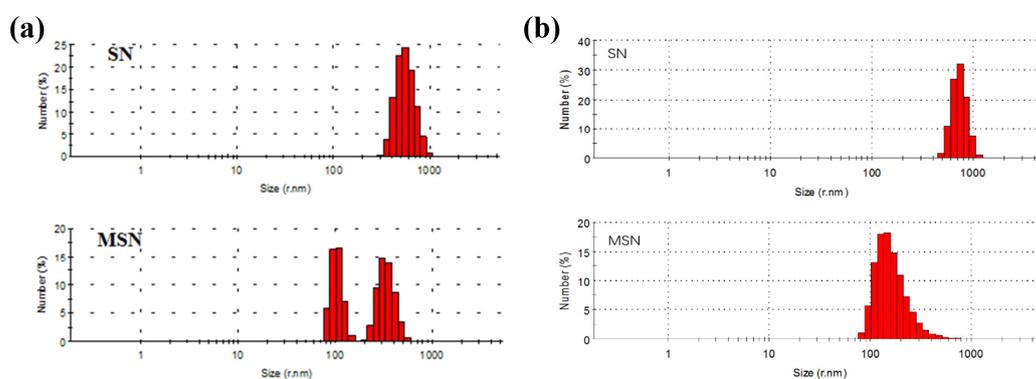


Figure 3. Hydrodynamic size distribution of silica and magnetic silica nanoparticles (a) before and (b) after removal of organic components.

3.2. Zeta Potential of Materials under Different Experimental Conditions

To further analyze the properties of the materials, the zeta potentials of silica and magnetic silica were examined under different preparation conditions (as shown in Figure 4). Figure 4a shows the zeta potentials of silica nanoparticles and magnetic silica nanoparticles prepared at different molar ratios of CTAB to PVP. It can be found that the potentials of silica are all higher than the potentials after loading with magnetic Fe_3O_4 (Figure 4c). The potential of the materials was greatest at a ratio of CTAB to PVP of 1:0.046. The zeta of the materials varied with different pH [35]. The zeta potentials of *Chlorella* sp. HQ as well as wrinkled magnetic silica nanoparticles at different pH values are shown in Figure 4b. *Chlorella* sp. HQ cell surfaces are usually negatively charged between pH 4 and 12 (Figure 4b). Magnetic silica nanoparticles also have a negative charge at neutral pH. Due to the CTAB coating, the nanomaterials have a positive zeta potential before calcination (Figure 4a). After calcination, the nanoparticles were all negatively charged, and different CTAB to PVP molar ratios had no significant effect on the zeta potential. Furthermore, as can be seen in Figure 4c, the removal of organic components via refluxing was not as effective as via calcination.

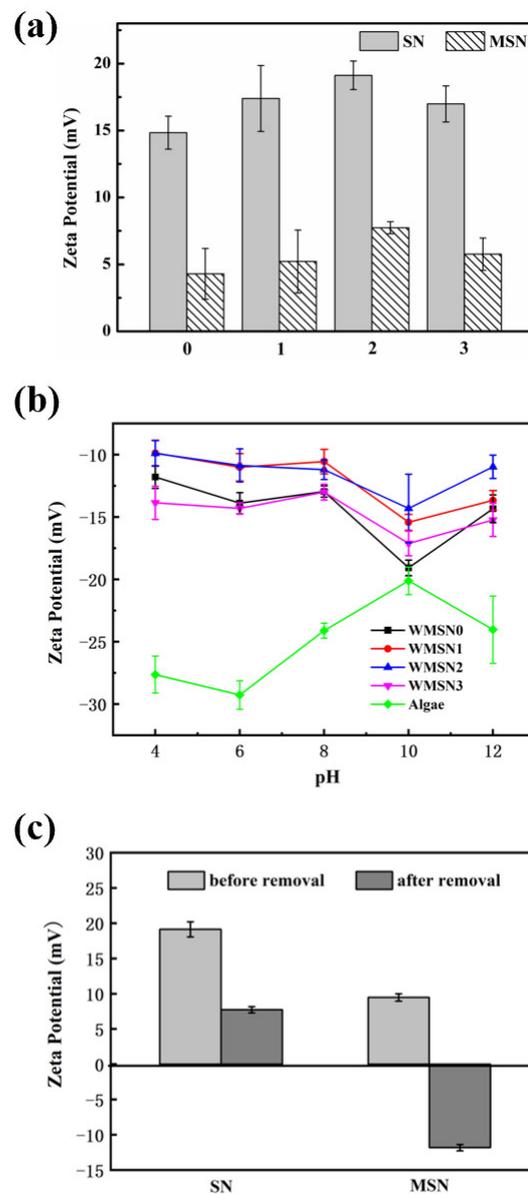


Figure 4. Zeta potential of (a) silica and magnetic silica nanoparticles with different molar ratios of CTAB: PVP; (b) wrinkled magnetic silica nanoparticles with different molar ratios of CTAB: PVP at different pH values; (c) Zeta potential of silica and magnetic silica nanoparticles before and after removal of organic components using different methods.

3.3. Harvesting of *Chlorella* under Magnetic Mesoporous Silica

3.3.1. Effect of Active Agent and Stabilizer Ratios on the Harvesting of *Chlorella*

To investigate the effect of the ratio of reactive agent stabilizer on the algae harvesting effect during the preparation of magnetic silica. The pH of the algal solution was 8, the reaction condition temperature was 25 °C, CTAB was used as the active agent in the reaction, and PVP was used as the stabilizer. Figure 5 shows the harvesting efficiency of Fe₃O₄ nanoparticles, magnetic silica nanoparticles, and folded magnetic silica for different molar ratios of CTAB to PVP on *Chlorella*. The nanomaterials exhibit different harvesting properties at different reactant molar ratios. Both before (Figure 5a) and after calcination (Figure 5b), the magnetic mesoporous silica materials showed better harvesting efficiency of *Chlorella* sp. HQ at larger ratios of stabilizer PVP, i.e., the harvesting efficiency increased with increasing PVP dosage [36]. This is because the particle size, surface morphology, and radial pore channels can be controlled by varying the molar ratio of CTAB to PVP [37]. The

particle size of nanoparticles decreased as the amount of PVP increased. The harvesting efficiency of *Chlorella* sp. HQ using magnetic silica nanoparticles and wrinkled magnetic silica nanoparticles were enhanced to some extent compared to Fe_3O_4 nanoparticles, but not significantly. At CTAB to PVP molar ratios of 1: (0, 0.023, 0.046, 0.092), the harvesting efficiency of MSNs for *Chlorella* sp. HQ was 53.01%, 56.73%, 61.65%, and 62.02%, respectively, while the harvesting efficiency of WMSNs for *Chlorella* sp. HQ was 54.58%, 59.49%, 62.28%, and 65.34%, respectively. Notably, the harvesting efficiency of positively charged magnetic silica nanoparticles was almost equal to that of negatively charged wrinkled magnetic silica nanoparticles.

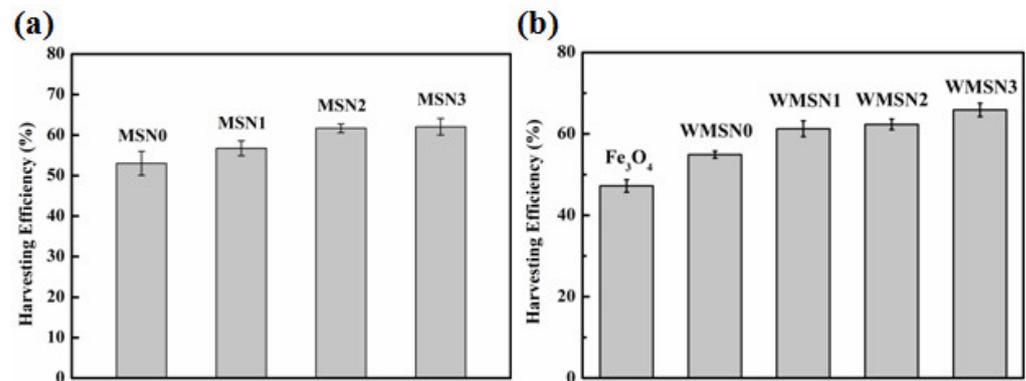


Figure 5. Harvesting efficiency of magnetic silica nanoparticles (a) before and (b) after being calcined with different molar ratios of CTAB: PVP at pH 8.0, 25 °C.

Previous studies have concluded that the mechanism of magnetic nanoparticles harvesting microalgae mainly includes adsorption electro-neutralization and adsorption bridging [11]. The outer cell surface of microalgae is distributed with a large number of functional groups, mainly hydroxyl, amine, carboxyl, and phosphate groups, which can dissociate in aqueous solution, and the cell surface thus carries a certain charge [38]. Microalgae cell surfaces usually possess a negative ζ -potential, which makes it possible to harvest algae using electrical neutralization [39]. Before the removal of the organic components, the positively charged surface of the MSNs would interact electrostatically with the negatively charged *Chlorella* sp. HQ. However, the magnetic silica material forms WMSNs after the removal of organic components, and its surface contains a large number of polar hydroxyl groups, and the electron pairs shared by hydrogen and oxygen atoms are biased towards the oxygen side, making its electron cloud large and prone to hydrogen bonding with the hydrogen atoms [40,41]. Bridging occurs between the WMSNs and the *Chlorella* sp. HQ cells, which makes the microalgae and the magnetic silica material bond more strongly [42]. However, the biochemical composition, species, and surface properties of the cell surfaces of different algal species are also different, and these differences can affect the harvesting efficiency of microalgae [43].

3.3.2. Effect of Mesoporous Structure Activator Removal Methods on the Harvesting of *Chlorella*

The active agents used in the preparation of magnetic silica were removed to promote the formation of the mesoporous structure of the material. It was found that the ethanol reflux method was more conducive to maintaining a stable structure of the material and resulted in a higher algal harvesting efficiency than the calcination method (Figure 6). At CTAB to PVP molar ratios of 1: (0, 0.023, 0.046, 0.092), the magnetic silica obtained using calcination yielded 54.9%, 61.2%, 62.3%, and 65.9% for *Chlorella* sp. HQ, while the magnetic silica obtained using ethanol reflux yielded 67.3%, 75.3%, 77.8%, and 83.7%, respectively. It was found that the harvesting efficiency of *Chlorella* sp. HQ increased by 12.4%, 14.1%, 15.5%, and 17.8%, respectively. It should be noted that although calcination methods could produce more porous structures, residual organic components via reflux methods

could promote algal harvesting (Figure 6). WMSNs played a major role in algal harvesting probably because of their wrinkled structures and incompletely removed CATB coatings.

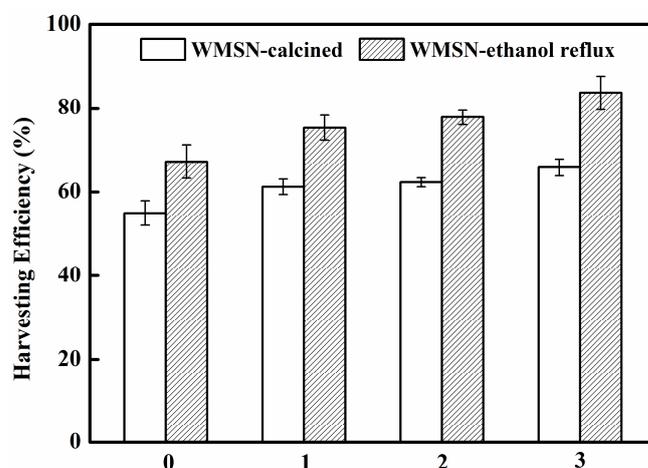


Figure 6. Harvesting efficiency of magnetic silica nanoparticles using different organic layer removal methods.

Zhao and Wang et al. [44,45] showed that the plant polyphenol (PP) surfactant has strong polar and hydrophilic groups, including hydroxyl, carboxyl, and ether bonds, and these functional groups not only improve the electrostatic stability of magnetic nanoparticles in the culture solution but also control the Fe_3O_4 particles to achieve different particle size distributions during nucleation and growth. CTAB, as a cationic surfactant, can bond with hydrogen in acid molecules via hydrogen bonding due to the lone pair of electrons in the nitrogen atoms in the molecule, resulting in a positively charged amino group, which is in agreement with the findings in Section 3.2. The structural basis of CTAB can promote the magnetic harvesting of *C. vulgaris* through adsorption bridging effects and electrostatic attraction [46,47]. Therefore, the best method for the removal of organic fractions was the ethanol reflux method, and the maximum harvesting efficiency of *Chlorella* sp. HQ was 83.7% at a molar ratio of CTAB to PVP of 1:0.092.

3.3.3. Effect of pH and Algal Concentration on the Harvesting of *Chlorella*

Exploring the effect of pH on the harvesting effectiveness of magnetic mesoporous silica materials for *Chlorella* (Figure 7), nanomaterials with different CTAB to PVP molar ratios showed similar harvesting performance. There were no major differences in the harvesting effect of magnetic mesoporous silica materials on microalgae at different pH values and algal concentrations. There was little difference in harvesting efficiency at pH 4 and 8, both being slightly greater than at pH 12. The harvesting efficiency of microalgae increased with the increasing PVP dosage. This demonstrated that the harvesting of *Chlorella* using magnetic silica is mainly due to the properties of the magnetic material and that environmental factors have less influence on the harvesting of microalgae. The harvesting efficiency of *Chlorella* sp. HQ increased by 11.7% (73.2% to 84.9%), 16.3% (67.3% to 83.7%), and 15.9% (59.2% to 75.1%) at pH 4, 8, and 12, respectively, when the molar ratio of the CTAB and PVP was increased from 1:0 to 1:0.092. And the harvesting efficiency increased by 16.4% (67.3% to 83.7%), 11.5% (72.7% to 84.2%), and 14.9% (69.2% to 84.1%) at algal densities of 0.2, 0.5, and 1 g/L, respectively. Between pH 4 and 12, both microalgae and magnetic mesoporous silica were negatively charged (Figure 4). Therefore, the mechanism of microalgae harvesting does not depend on charge neutralization in this work, but mainly on adsorption bridging through the interaction between the magnetic silica material and the microalgae functional groups. At the same time, the presence of locally positively charged functional groups on the surface of algal cells is electrostatically attracted to microalgal cells, such as protonated amino- NH_3^+ (membrane glycoproteins or

other compounds) [48]. Secondly, the presence of -OH groups in the silica layer on magnetic nanoparticles also promotes electrostatic attraction with positively charged functional groups on microalgae [49]. Therefore, the optimal pH for the harvesting of *Chlorella* was 4, the algal concentration was 0.5 g/L, and the molar ratio of CTAB and PVP was 1:0.092, with a maximum harvesting efficiency of 84.2% for *Chlorella* sp. HQ.

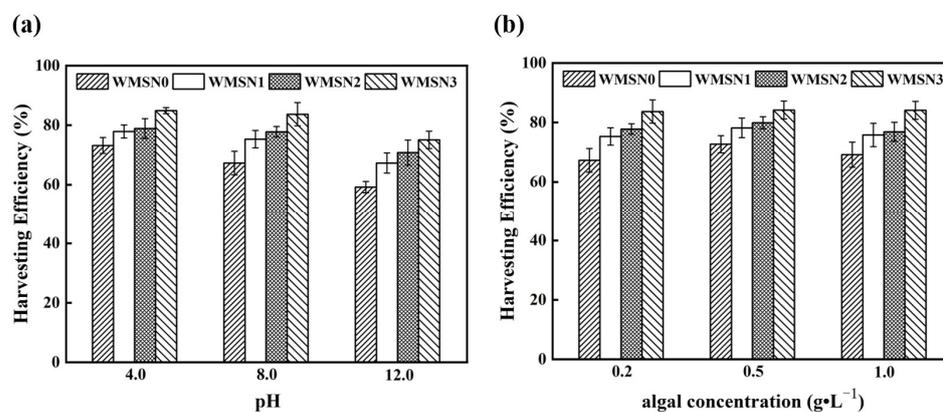


Figure 7. Harvesting efficiency of wrinkled magnetic silica nanoparticles with different reactant molar ratios at different (a) pH values and (b) algal concentrations.

4. Conclusions

In this work, magnetic silica nanomaterials were prepared using the co-precipitation method using Fe_3O_4 as a carrier, and the effect of magnetic silica on the harvesting of *Chlorella* sp. HQ was investigated. The dispersion of the material was better after the coating of magnetic Fe_3O_4 microspheres with the silicon dioxide layer. The organic components on the surface of the material were removed via calcination and ethanol refluxing, and TEM showed that the porous structure of the magnetic silica nanoparticles was more obvious after the calcination treatment, but the residual organic components using the refluxing method could promote the harvesting of microalgae. Different ratios of reactive agent CTAB and stabilizer PVP resulted in different harvesting efficiencies of the materials for microalgae. The maximum harvesting efficiency of *Chlorella* sp. HQ was 84.2% when the ratio of CTAB: PVP was 1:0.092, the solution of pH was 4, and the algal concentration was 0.5 g/L. The mechanism of harvesting microalgae using magnetic silica mainly includes adsorption electro-neutralization and adsorption bridging. Meanwhile, the local presence of positively charged functional groups on the surface of algal cells and the electrostatic attraction of magnetic mesoporous silica would also promote the harvesting of microalgae. This magnetic harvesting technology has great potential and application prospects in microalgae harvesting and bloom control.

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