Journal of Hazardous Materials 324 (2017) 498–506

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Removal of harmful alga, *Chattonella marina*, by recyclable natural magnetic sphalerite

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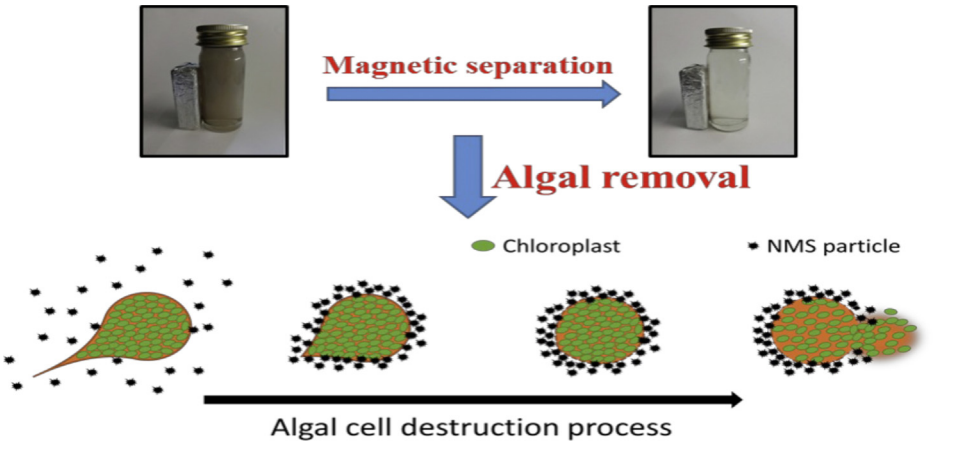
HIGHLIGHTS

- First report on removal of *Chattonella marina* by natural magnetic sphalerite (NMS).
- NMS (1–2 g/L) could remove *C. marina* rapidly and efficiently.
- Temperature > 25 °C, salinity > 30 ppt and pH value < 7.5 enhanced algal removal.
- Adsorption and physical interaction lead to cell morphology change and removal.
- NMS exhibited excellent stability after magnetic recycling and repeated use.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 16 July 2016
Received in revised form 22 October 2016
Accepted 7 November 2016
Available online 9 November 2016

Keywords:
Harmful algal blooms
Chattonella marina
Natural magnetic sphalerite
Recyclable

ABSTRACT

Fish-killing harmful algal blooms (HABs) of *Chattonella marina* causes serious hazards and risks to fish farming and environment throughout the world. At present, it is necessary to explore cost-effective and recyclable materials for controlling *C. marina* blooms to reduce the cost and control the potential side effect to the environment. A novel earth-abundant natural magnetic sphalerite (NMS) for removing *C. marina* was systematically investigated, including the effect of NMS dosage, temperature, pH and salinity on algal removal efficiency. Algal cells could be rapidly removed by NMS (1–2 g/L) through adsorption and physical interaction. The algal destruction process was enhanced under the following reaction conditions: temperature > 25 °C, salinity > 30 ppt and pH value < 7.5. The reusability of magnetic recycled NMS and effect of light irradiation on algal cell removal were also determined. NMS exhibited excellent stability after repeated algal cell removal, and the efficiency was further enhanced by light illumination. The current study suggested that using NMS to control *C. marina* blooms could be a novel promising strategy, which is cost-effective, stable, and easy for recycling.

1. Introduction

Over the past few decades, harmful algal blooms (HABs) have brought more and more serious negative impacts to public health,

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http://dx.doi.org/10.1016/j.jhazmat.2016.11.018
0304-3894/

fisheries, tourism and ecosystem [1]. HABs can lead to undesirable color and smell change of water body, large scale mortalities of fishes, toxic contamination of filter-feeding organisms and a compromised life quality for consumers [2]. *Chattonella marina* is a notorious marine fish-killing Raphidophyceae species which caused severe hazard and risks to fish farming and environment [3]. This harmful alga could be trapped and clogged in fish gill mucus, which leads to gill cell necrosis and finally the suffocation of fish [4,5]. Numerous *C. marina* associated accidents have been reported during the last 60 years with a worldwide distribution, causing huge economic losses and environmental impacts in India [6], Korea [7], Japan [8], Australia [9], America [10] and China [11]. With the current trend of seawater pollution and eutrophication, the coastal regions worldwide will encounter increasing frequency of *C. marina* blooming events. If there is not efficient solution, the mariculture industries will keep suffering from economic losses and fisheries resources impacts in the future.

In order to prevent severe impacts to fishery economics and the environment, high performance of algal removing methods for *C. marina* are required. Traditional chemicals such as copper sulfate and strong oxidants have been abandoned due to the high-cost, unspecific toxicity to marine organisms and significant collateral damage to the environment [12]. Although novel chemicals including thiazolidinedione [13], cypermethrin [14] and prodigiosin [15] have shown good algal removal performance on *C. marina*, the complexity of synthetic process with high cost is still a major limitation on the use of these chemicals. Bacteria such as *Shewanella* sp. [16], marine actinomycete [17], *Bacillus* sp. [18] and *Pseudoalteromonas haloplanktis* [19] have exhibited different levels of algicidal abilities. However, the feasibility of growing and applying a large quantity of algicidal bacterial biomass for suppressing algal bloom should be taken into serious consideration. Natural clays (NC) and modified clays (MC) have attracted relatively more attentions as powerful means for controlling HABs in recent 20 years, owing to their good adsorption to algal cells [20,21]. However, there are several critical problems remained in terms of applying clays on harmful algal removal. The settled large amount of clays and adsorbed harmful algae on sea bottom may cause substrate effects, feeding disturbance, suffocation or burial of clams [22]. Besides, clay modifying process increased the material pretreating complexity and cost, and it is hard to evaluate the effect of doped chemicals and other artificial additives from the modified clays on benthic organisms [12]. Furthermore, in the current clay applications, the materials are hardly recycled for repeated use, which further increases the cost.

In recent years, several mineral samples have been reported to have good adsorption abilities [23–25], while some even have magnetic property [26,27]. The possibility of using these magnetic recyclable minerals on harmful algal removal is of great interest. Natural magnetic sphalerite (NMS) is a naturally occurring and earth-abundant mineral, which can be easily obtained from lead-zinc mines around the world. NMS has been reported to possess great adsorption ability with strong magnetic property for easy materials recycling [28]. Besides, when provided with appropriate visible light irradiation, NMS exhibited good photocatalytic activity [28]. The mineral has been successfully applied in photocatalytic reduction of metal ions, degradation of azo dyes and inactivation of bacteria [28–31]. The excellent characteristics make it reasonable to associate NMS with a novel recyclable algal removal strategy for harmful algae like *C. marina*. Therefore, it is necessary to evaluate the probability and feasibility of developing a NMS based algal removal technology.

In present study, the removal of *C. marina* by NMS was systematically studied. A set of parallel experiments were designed to investigate the effect of material dosage, temperature, salinity and pH on the harmful algal removal efficiency of NMS. The major mechanism for the destruction of *C. marina* by NMS was also investigated and discussed. A multi-cycle runs experiment was performed to test the reusability and stability of NMS. Finally, removal of *C. marina* by NMS was conducted under light irradiation to simulate the practical situation.

2. Materials and methods

2.1. Materials preparation and characterization

The sample of natural magnetic sphalerite (NMS) was obtained from a mining site in China as previously described [28]. Prior to usage, the raw NMS particles were sieved (pores size <38 μm) and then washed for several times by ethanol and ultra-pure water. X-ray diffraction (XRD) pattern of the NMS sample was obtained by a DMAX-2400 X-ray diffractometer (Rigaku, Japan). The morphology of NMS was observed by a scanning electron microscope (SEM, FEI Quanta 400 F, USA) at 10 kV. A vibrating sample magnetometer (VSM-7300, Quantum design, Lakeshore, USA) was used to determine the magnetic property of NMS powders. A surface area and porosity analyzer (Micromeritics ASAP2020, USA) was utilized for measuring the Brunauer-Emmett-Teller (BET) surface area of NMS sample.

2.2. Algal culture

The *C. marina* (CCMA-196) used in this study was purchased from the Center for Collections of Marine Algae of Xiamen University, China. Algal cultures were grown and maintained at 25 ± 1 °C in f/2 medium without silica [32]. The medium was prepared in sterilized natural seawater with a salinity of 30 at pH 7.5. A 12/12 h light-dark cycle with 3000 lx of light intensity was provided by cool-white 8 W fluorescent lamps (RSN-T4/8W, Raysnow, China). Algal cells were daily counted by a hemocytometer (Cambridge Instruments Inc., USA) under a light microscopy (E220, Nikon, Japan). The algal cells at early stationary growth stage were used for experiment.

2.3. Exposure of C. marina to NMS under different physico-chemical conditions

For all experiments in this study, the initial *C. marina* cell density was adjusted to 5.0×10^6 cells/L, which is a typical level found in *C. marina* algal blooms [33,34]. To study the dosage effect, toxicity of added NMS concentration to *C. marina* and two additional aquatic algae *Chlorella* sp. and *Synechococcus* sp. were tested prior to setting the experimental concentration (Supporting information). Different volumes of NMS stock dispersion (100 g/L) were added into *C. marina* cultures (at 25 °C) to set the final concentrations to 0, 0.5, 1.0, 1.5 and 2.0 g/L, respectively. Each NMS-algal culture was mixed and vigorously stirred by a plastic stirrer at 250 rpm. At fixed time intervals, an aliquot of 0.1 mL of suspension was collected for counting the algal cells under a light microscope equipped with a CCD camera (UT340, 10 moons, China) in triplicate. The algal removal experiment was performed for 12 h to provide sufficient time to reach the equilibrium of the reaction.

Parallel experiments were also conducted to study the algal removal efficiency of 1 g/L NMS as a function of temperature, salinity and initial solution pH value. The temperature was adjusted to 15, 20, 25, 30 and 35 °C respectively, by a temperature-controlled incubator (LM-570RD, Yihder, Taiwan). The salinity was adjusted to 25, 30, 35, 40 and 45 ppt (parts per thousand), respectively, measured by a refractometer (A366ATC, Vista, China). The pH value of the solution was adjusted to 5.5, 6.5, 7.5, 8.5 and 9.5, respectively with 1 M HCl and NaOH, measured by a pH meter (Thermo Orion