



Preparation of martite nanoparticles through high-energy planetary ball milling and its application toward simultaneous catalytic ozonation of two green algae



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ABSTRACT

The efficiency of heterogeneous catalytic ozonation in the presence of martite nanocatalyst was studied as a novel method for the thorough and in situ removal of *Oocystis sp* and *Cosmarium sp* green algae. High-energy planetary ball milling was utilized to prepare martite nanoparticles (MNPs) from natural martite particles (NMPs). X-ray diffraction (XRD), scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FT-IR) analysis, X-ray photoelectron spectroscopy (XPS), and Brunauer–Emmett–Teller (BET) were carried out to determine the physical and chemical characteristics of NMPs, and MNPs. The mechanism of heterogeneous catalytic ozonation was investigated in the presence of different reactive oxygen species (ROSs) scavengers. The degradation process was accomplished via the continuous attacks of hydroxyl radicals ($\bullet\text{OH}$) and superoxide radicals ($\text{O}_2^{\bullet-}$). The variation of chlorophyll-a concentration and the morphologies of the algae cells were investigated. The results obtained from chlorophyll-a content, light microscopic and SEM images revealed the complete degradation of the algae cells. Moreover, the main elements of algae structure and intermediates, generated during the degradation process were identified using EDX and GC–MS analysis. The mineralization efficiency of the proposed catalytic ozonation process was investigated using of COD results.

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1. Introduction

Algal bloom is caused by excessive growth of algae in the presence of enough nutrient, sunlight, and suitable temperature which is becoming more frequent and problematic in waterbodies. The harmful effects of the algal bloom are divided into toxic and high biomass producers [1]. The harmful algal blooms, such as green algal blooms, which are generated by high biomass producers interrupt the water treatment process by inducing low filter performance, increasing the growth of the microorganisms in the distribution systems, and raising coagulant consumption. Moreover, their specific effects on water taste and odor, turbidity, disinfection by-products (DBPs), and hypoxia induction has led to concerns over the public health consequences of this group [2].

On this basis, the removal of various genera of algae from waterbodies is of great importance. Recently, advanced oxidation pro-

cesses (AOPs) have been noticeably considered for removal of various genera of algae and their toxins via hydroxyl radicals. Among the AOPs, ozonation process has been introduced as an effective and simple technique for water treatment because of some reasons: (1) generation of less harmful by-products (compared to the chlorine), (2) fast removal of microorganisms and pollutants, (3) prevention of secondary pollution (compared to the coagulant agent), and (4) complete decomposition of the compounds released from the algae membrane disruption which are resistant to natural destruction and biodegradation [3]. However, regarding the imperfect degradation of pollutants and low stability of ozone, the application of ozonation may not be considered cost-effective. In this context, the process of heterogeneous catalytic ozonation using solid catalysts and producing hydroxyl radicals of high oxidation potential has been a promising advanced oxidation method. Reusability and prevention of further pollution to the system are some advantages of using heterogeneous catalysts [4].

In the present research, the potential of the heterogeneous catalytic ozonation in the presence of natural iron-based nanocatalysts, such as martite was evaluated as a novel process for the synchronic removal of *Oocystis sp* and *Cosmarium sp* algae. *Oocystis*

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sp and *Cosmarium sp* are the genera of the respectively *Oocystaceae* and *Desmidiaceae* family [5,6]. The mentioned algae in comparison with the other species, had a great growth in the Nahand dam of East Azerbaijan in Iran, from which the samples were gotten. In other words, algal bloom was made due to the higher growth of the indicated algal cells, which could produce unpleasant odor, taste, color, and requiring extra removal steps for processing of drinking water. Although algae cells were inactivated during water purification processes, the dead cells of mentioned algae still caused filter blockages in filtration processes. Therefore, the thorough removal of these algal species were of great importance. According to literature studies, there is no reported work on the removal of *Oocystis sp* and *Cosmarium sp* genera by heterogeneous catalytic ozonation using MNPs as the catalyst of the process. So, this is the first time in which the mixture of algae degradation is investigated under the operated conditions via catalytic ozonation process. Moreover, utilizing other processes like filtration process might face with some problems like the blockage of the filters and finally the decrease of the treatment performance. Due to the higher production of hydroxyl radicals and the capability of the process to degrade large quantities of the algal cells in a short time and without any remained part of the algal cells, application of heterogeneous catalytic ozonation was regarded cost-effective, rather than using single ozonation process. Martite is one of the most abundant natural mineral on the surface of earth and is regarded as a potential heterogeneous iron based catalyst for various degradation processes. Moreover, it is cheap and has no effect on environmental pollution. In spite of the inferred novel features for natural martite, there are still some disadvantages. One of them attributes to the large size of the particles and lower specific surface area of NMPs. This issue affects the mass transport phenomenon in the catalytic systems. These mentioned disadvantages confines the use of NMPs as the catalyst of processes. So, the size of its particles should be reduced from micron scale to nano scale in order to prepare more active sites on the catalyst which leads to the higher performance of the catalyst in the process. High energy planetary ball mill which is for synthesis of nanomaterials has recently gained main attention over the conventional synthesis methods. It is a simple and leads to the green production of large value of nanoparticles in a short time and in the ambient temperature [7]. So, in the present work, high-energy planetary ball milling method was used to reduce the size of NMPs into nano-sized one.

In order to examine the physical and chemical characteristics of NMPs and MNPs, the X-ray diffraction (XRD), Scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), and Brunauer–Emmett–Teller (BET) analyses were fulfilled. Then, the synergistic effect of the heterogeneous catalytic ozonation was assessed. Subsequently, the effects of the main operational parameters namely ozone gas inlet flow rate, catalyst concentration, pH, and density of algae were investigated on the simultaneous removal of algae in the water. Afterwards, the concentrations of the dissolved ozone and oxygen were determined in the absence and presence of algae cells to assess the mechanism of the ozonation process during algae removal. In the next step, the effects of different reactive oxygen species (ROs) scavengers on the removal efficiency of the algal cells were evaluated for precise investigation of the process mechanism. Furthermore, the content of chlorophyll-a was assessed during the degradation process to evaluate the effectiveness of the heterogeneous catalytic ozonation process. SEM and light microscopic images were used to study the morphology of the algae. Finally, the degradation intermediates produced during the catalytic ozonation of algae were identified using GC–MS method.

2. Materials and methods

2.1. Algal culturing

The green alga suspension was obtained from Nahand dam in the East Azerbaijan, Iran, and cultivated for the experiments of the present research. The algal suspension of *Oocystis sp* and *Cosmarium sp* was cultured in distilled water at 25 °C and enriched with Beijerinck culture medium [8]. The cultivation method accomplished in the presence of 200 lx of white fluorescence light and using 12:12 h light: dark cycle. Then, the cultivated samples were subcultured and stored at room temperature (25 °C) and shaken manually once in a day. The alteration in the algal density was evaluated daily by a microscope (Olympus CH-2) and a hemocytometer. Subsequently, the samples were transferred to a large container and unified to be used in the experiments.

2.2. Counting the algal cells and measuring chlorophyll-a content

A hemocytometer was used to monitor the algal density variation. There were 9 large squares in haemocytometer, among which the middle square contains the main area for algal counting. Similar to others, the middle square constituted of 400 grids that 80 grids were chosen to be as the counting area. As the depth of the grids was 0.1 mm, for getting the content of 1 mm³, it was multiplied with 10. Each algal suspension was placed in the counting area, then by the assistance of a microscope the total viable cells were counted. Coordinately, the algal density was calculated using Eq. (1):

$$\rho = \frac{V}{80} \times 400 \times 10^4 \times f \quad (1)$$

where ρ is the algal density (cells/mL), v signifies the number of algal cells in 80 counting grids; 400 is the whole number of grids within the hemocytometer; 10^4 is the conversion factor for the volume; and f is the dilution factor [2].

In order to measure chlorophyll-a content briefly, 50 mL of algal samples after 5, 10, 15 and 20 min of catalytic ozonation process were filtered and homogenated by 100% acetone. After extraction and centrifugation (10 min at 3000 r/min), absorbance spectra was determined using a UV–vis spectrophotometer (Lightwave S2000, England) at the maximum wavelength of 661–665 nm. Finally, the pigment concentration was calculated by using the equations described by Lichtenthaler [9] as follows: Chlorophyll-a concentration = $(11.75A_{661.6} - 2.35A_{664.8})$

2.3. Planetary ball milling procedure

Natural martite, hematite pseudo morphs after magnetite [7], was provided from Sangan mine (Mashhad, Iran). The jaw and cone crushers (Geological survey of Iran) were used to crunch martite to the range of 0.5–2 cm. Then, a rod and ball milling (Kian Madan Pars Co, Iran) were employed for further crushing the sample to form micro- martite particles between the range of 30 and 50 μ m. Lastly, a high energy planetary ball mill (Retsch, Model PM 400, Germany) was performed to reduce the size of NMPs into the nano-range. The ball-mass to powder-mass ratio of 10:1 was chosen to produce the nanoparticles. Also, the milling was fulfilled at the rotation speed of 320 rpm. At time intervals of 2 h the produced nanoparticules were withdrawn.

2.4. Characterization of the martite samples

In order to identify the crystal structure, XRD analysis was applied (PANalytical X' Pert PRO, Germany). XRD analysis was used to samples with CuK α radiation (45 kV, 40 mA, 0.15406 nm).

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