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Removal of diatom *Nitzschia* sp. cells via ozonation process catalyzed by martite nanoparticles

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ABSTRACT

Martite nanoparticles (MNPs) catalyzed ozonation process was utilized for rapid and effective degradation of diatom *Nitzschia* sp. cells. MNPs were produced using high-energy planetary ball milling technique from the natural martite particles (NMPs). Complete examination of the physical and chemical characteristics of NMPs, and MNPs were carried out by investigating 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), Brunauer–Emmett–Teller (BET) and atomic absorption spectroscopy (AAS) analyses. The role of MNPs was investigated by XPS analysis, calculating the synergistic factor, and monitoring the dissolved concentration of ozone and oxygen. The decreased dissolved ozone concentration and increased oxygen concentration accompanied with the increased synergistic factor confirmed the positive role of Fe^{2+} and Fe^{3+} species in MNPs. The progress of the process through indirect mechanism was determined using simple organic and inorganic compounds acting as ROSs scavengers. Accordingly, the process for the diatom removal was mainly fulfilled by successive attacks hydroxyl radicals ($^{\bullet}OH$) and superoxide radicals ($O_2^{-\bullet}$). For identifying the effectiveness of the MNPs catalyzed ozonation process, the light microscopic along with SEM images, variation of chlorophyll-a concentration, GC–MS and COD analyses were studied. The results confirmed the destruction of complex structure of diatom cells to the simple structures. Also, the results proved the simultaneous degradation of diatom cells and their chlorophyll a content in the reaction media indicating the effectiveness of this process in comparison with other studied processes.

1. Introduction

Diatoms are microscopic algae, which are known to have a siliceous coverage, called frustule. Diatoms live in all kind of superficial waters. Diatom blooms arise in specific months, leading to unpleasant taint and odor to the freshwater and blocking filtration systems of treatment processes (Chen et al., 2009). Therefore, the removal of diatom bloom from water-bodies is of great importance. The treatment of algal blooms was accomplished by using activated carbon (Falconer et al., 1989), chlorination (Shen et al., 2011), filtration (Naghavi and Malone, 1986), and biological (Bourne et al., 2006) methods. It is worth to mention that the degradation of diatoms accomplished in two steps including degradation of the frustules and then the compounds inside the siliceous frustule (Barrett et al., 1996; Martin and de los Reyes Fernandez, 2012). The usage of abovementioned processes reported to be not effective, since these treatment methods were unable in successful degradation of frustules (Akcil and Koldas, 2006; Jančula et al., 2014; Rubio et al., 2002). The lower performance of these processes for algal removal may because the filter blockage due to the higher diatom concentration, production of toxic byproducts in the chlorination process, higher reaction time requirement in biological processes, and imperfect degradation of diatom cells (Jančula and Maršálek, 2011; Wang et al., 2016). Recently, advanced oxidation processes (AOPs) such as ultrasound, photocatalytic oxidation, and ozonation process have attracted discernible consideration for the removal of various genera of algae and their toxins (Feitz et al., 1999; Mahmoodi et al., 2010; Purcell et al., 2013). Among the various AOPs, ozonation process of high oxidation potential is a proven powerful method (Yuan et al., 2013). However, the selective degradation of pollutants and low stability of ozone, restricted the wide application of ozonation alone. Thereby, the process of

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catalytic ozonation process using solid nanocatalysts has been a promising advanced oxidation method due to the production of higher amounts of hydroxyl radicals (Khataee et al., 2016b). Reusability and prevention of further pollution to the system are some advantages of using nanocatalysts (Khataee et al., 2016c). Thereby, catalytic ozonation process was regarded as a cost-effective process due to the higher production of hydroxyl radicals and the capability of the process to degrade large quantities of the green algal cells in a short time and without any residual (Khataee et al., 2018; Wu et al., 2011).

In the present paper, the potential of the MNPs catalyzed ozonation process was assessed for the removal of the cells of diatom *Nitzschia* sp. *Nitzschia* sp. is the genera of Bacillariaceae family (Ding et al., 2017). *Nitzschia* sp. as a genus of diatoms showed a great growth in comparison with the other species in the Nahand dam of East Azerbijan (Iran). The higher growth of the *Nitzschia* sp. cells led to the generation of diatom bloom, which was the source of some problems such as unpleasant odor, taste, color, and neurotoxin responsible for the human illness (Kotaki et al., 2000). Therefore, this phenomenon creates the significance of the diatom removal from the contaminated water-bodies. According to literature studies, there is no reported work on the comprehensive removal of any diatom species by MNPs catalyzed ozonation process. Thereby, this is the first study on *Nitzschia* sp. diatom degradation under the operated conditions via MNPs catalyzed ozonation. Martite (Fe_2O_3) is one of the most abundant natural minerals on the surface of earth which is cheap and has no effect on environmental pollution. More recently, it was reported as a profitable heterogeneous iron based catalyst for different catalytic processes such as degradation ones (Khataee et al., 2017b, 2018; Rahmani et al., 2016). Moreover, about the formation of martite from magnetite and hematite ores it is worth to mention that redox and non-redox reactions cause pseudomorphic replacement of hematite by magnetite and magnetite by hematite. The pseudomorphic replacement of magnetite by hematite due to oxidation results in the newly structured hematite known as martite. Martite is a stable intermediate during the transformation of magnetite to hematite which is known as martitization phenomenon in literature (Mücke and Cabral, 2005). Despite the novel features of natural martite, some disadvantages such as large size of the NMPs and consequently lower specific surface area lead to some limitations for their usage in the degradation processes. Therefore, the size reduction of NMPs is required in order to enhance the catalyst performance in the process. Recently, the hydrothermal process, and the chemical methods were used for synthesing nanocatalysts. The use of these processes were restricted due to their toxic and time consuming aspects (Reijnders, 2006; Robertson, 1996; Yan et al., 2014). High energy planetary ball milling is one of the green synthesis procedures of nanocatalysts. This method has recently attracted the attention of most of the researches because of its simplicity and green production of large value of nanoparticles in a short time and in the media temperature. Many researchers produced martite nanoparticles by using high energy planetary ball milling (Rahmani et al., 2016). In a recently published work, the researchers investigated the catalytic performance of martite nanoparticles in heterogeneous Fenton-like (Rahmani et al., 2016), and heterogeneous sono-Fenton-like processes (Dindarsafa et al., 2017) for degradation of various textile dyes. In these studies, in comparison with natural martite sample, MNPs were able to provide a surface in nanoscale for increasing the removal efficiency. Indeed, the overall purpose of previous studies was to investigate the catalytic performance of martite nanoparticles and the role of martite catalyst and the iron ions were not assessed in detail. In the present paper, high-energy planetary ball milling method was used to produce MNPs. Then, the nano-sized catalysts were made after 2, 4, 6 h of high-energy planetary ball milling method. The physical and chemical characteristics of NMPs, and MNPs were investigated by XRD, SEM, EDX, FT-IR, XPS, and BET analysis. As mentioned before, there are some research studies on the removal of algal cells (Wu et al., 2011). However, there is no comprehensive study on the utilization of catalytic ozonation process for the removal of diatom cells. In our previous study (Khataee et al., 2018), the catalytic ozonation process was used for removal of green algal cells and there was not any study on investigating the role of Fe^{2+} and Fe^{3+} for the removal of algal cells. In contrast, the novelty of this study was to use the catalytic ozonation process for the removal of diatom cells which were poisonous in comparison with green algal cells. Moreover, the significant purpose of this study was to investigate the main role of MNPs as the catalyst containing Fe^{2+} and Fe^{3+} species by calculating the synergy factor and monitoring the dissolved ozone and oxygen concentration in the absence and presence of the diatom cells. Investigating the effectiveness of the MNPs catalyzed ozonation process via different analyses such as SEM and microscopic images, GC-MS and COD results were the other significance of the present work. Afterwards, the effects of the main operational parameters such as catalyst concentration, ozone gas inlet flow rate, pH, and density of algae were investigated on the diatom removal efficiency in water. Subsequently, for further and precise evaluation of the main oxidizing species and the mechanism of MNPs catalyzed ozonation process, various organic ROSs scavengers were utilized. Moreover, the effectiveness of the MNPs catalyzed ozonation process in rapid and complete degradation of the diatom bloom, were evaluated by assessing the variation of chlorophyll-a content, SEM and light microscopic images of the destroyed diatom cells, and the results of GC-MS analysis.

2. Materials and methods

2.1. Diatom culturing

Nitzschia sp. was obtained from Nahand dam in the East Azerbaijan, Iran. Diatoms were inoculated into 500 mL f/2 medium. The main samples for the experiments were conducted in 250 mL Erlenmeyer flasks containing 50 mL f/2 medium (Guillard, 1975). Then, the flasks were incubated with a fluorescence light intensity of 200 lux at 25 °C for 15 days. The samples were sub-cultured and kept at room temperature (25 °C) and shaken manually once in a day. The alteration of diatom cell suspension density was monitored daily by a microscope (Olympus CH-2) and a hemocytometer slide. Finally, the samples were unified by transferring to a large container in order to be used in the various experiments.

2.2. Counting the diatom cells

The diatom cell counting was conducted by using a hemocytometer. After placing the diatom suspension in the counting chamber, a microscope was utilized to count the total viable cells. Thereby, Eq. (1) was used to calculate the diatom density before, and after 5,10,15,20 min of MNPs catalyzed ozonation process.

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

where ρ signifies the diatom density (cells/mL), v is the number of diatom 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 (Wu et al., 2012).