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Self-immobilization of a magnetic biosorbent and magnetic induction heated dye adsorption processes

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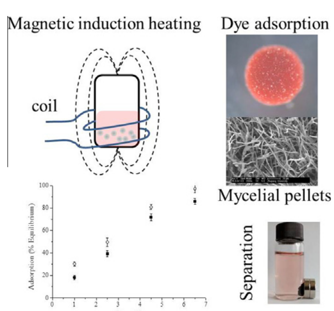
HIGHLIGHTS

- A fungus with strong self-immobilization ability was used for dye adsorption.
- The fungus can form magnetic pellets during self-immobilization.
- Temperature can be remotely controlled via magnetic induction heating.
- Energy saving, easy separation and higher adsorption rates can be achieved.

GRAPHICAL ABSTRACT



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ABSTRACT

Biosorbents for wastewater treatments is one of the most widely studied techniques in environmental and bioresource research. A marine-derived *Penicillium janthinellum* strain fungus was used in this study to prepare self-immobilized mycelial pellets. Fe_3O_4 nanoparticles were added in the culturing media, which were automatically incorporated in the mycelial pellets during culturing process to endow the pellets with magnetic properties. These magnetic mycelial pellets were used as biosorbents for water treatments, and their morphology was characterized by microscopic observation, Energy dispersive X-ray analysis, Fourier transform infrared spectroscopy and thermal gravimetric analysis. The effects of nanoparticles in culture media on pellet formation were discussed and the content of nanoparticle in culturing media was optimized. Study on Congo red adsorption from aqueous solutions showed that the pellets with 71.6 wt% Fe_3O_4 nanoparticles had a maximum adsorption capacity of 102.4 mg/g pellets (360.6 mg/g mycelia), and the solution heated by magnetic induction showed faster adsorption rates than that of bulk liquid heating processes under the same adsorption temperature. These pellets were easily separated by magnetic forces and the magnetic induction heating is beneficial in energy saving when comparing to traditional heating processes.

1. Introduction

Water pollution is a severe problem in many regions. Reports show that around 300–500 million tonnes of wastes including heavy metal ions, dyes and other contaminants are released into water systems annually, and it is predicted that one third of the world population would experience clean water problems by 2030 [1]. A variety of water treatment techniques using physico-chemical and biological processes have been applied [2], while ion-exchange resins and activated carbons are still recognized as two of the most effective and convenient adsorbents for waters containing adsorptive pollutants [3]. However, their high cost is a major limitation for large scale usage in industries.

Many solid porous materials have heavy metal ion or dye adsorption abilities. Therefore, natural materials such as clay, ash

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and various biomasses have been investigated as cheap adsorbents for water treatments, with some showed high efficiency [4,5]. Volesky [6] defined biosorption as the property of certain biomolecules or biomasses to bind and concentrate selected ions or molecules from aqueous solutions. It is mainly based on the affinity between biosorbents and adsorptive pollutants, which is usually due to the functional groups such as sulfonate, phosphonate and amine existed on the surface of biomass materials [6]. With over 3000 research articles and hundreds of biosorbents published [3,7], fungi, algae and agricultural wastes are the most widely studied biomasses currently. Both living and dead microorganisms have been used in research. However, because living ones usually need nutrients and certain maintenance and growing environments, dead microorganisms are preferred in many cases [8], but living ones may be used for some specific applications. Meanwhile, many biosorbents used are in suspended forms, which may be not effective and make the post separation of these biomasses from treated water extremely difficult [9]. Moreover, those biomasses left in the water may cause secondary pollution. This problem also limits the application of many biosorbents in industrial scale.

In order to overcome this drawback, some research used immobilized microorganisms as biosorbents for easy separation [10]. Magnetic collection is also an easy and efficient way to separate adsorbents and iron oxide nanomaterials have been widely studied for wasterwater treatment [11]. Pavía-Sanders et al. [12] prepared some magnetic polymer nanoparticles for crude oil recovery which featured easy collection by magnetic force. Jiang et al. [13] used magnetic chitosan beads for copper removal from aqueous solutions, and their results showed that by embedding Fe_3O_4 nanoparticles as bead core, the biosorbent particles can be separated in less than one minute from water solution with a low magnetic field. Zhang et al. [14] prepared snowflake-like $ZnO–SiO_2–Fe_3O_4/C$ composites for the application of adsorbing heavy metal ions and organic pollutants. They found that the Fe_3O_4/C coating can facilitate the separation of adsorbents for subsequent usage. In addition, the combination of magnetic nanoparticles with various immobilized biosorbents can form hybrid adsorbents with other magnetic-responsive properties, such as magnetic induction heating [15]. Schmidt [16] synthesized Fe_3O_4/poly(ε-caprolactone) hybrid particles with a core–shell structure. The magnetic core can be heated up via magnetic induction which caused a thermal transition of the polymer shell. Štěpánek et al. [17–19] prepared different magnetic particle containing beads for volatile organic compounds adsorption/desorption and chemical release studies. The results showed that the temperature inside the magnetic beads can be remotely controlled which is convenient for many applications. This temperature controlling feature is also useful for pollutant adsorption, as temperature is a vital factor in adsorption processes. Therefore, immobilized adsorbents with magnetic inducible properties may be good candidates for water treatments.

In this study, a marine-derived *Penicillium janthinellum* strain fungus was used for dye adsorption from aqueous solutions. This fungus had strong pellet forming ability even with high concentrations of particles in culture media. Magnetic mycelial pellets were prepared by adding Fe_3O_4 nanoparticles in culture media, which can be imbedded into the mycelial pellets during hyphal growth. Properties of the self-immobilized biosorbent were characterized, and the dye adsorption capacity was investigated with adsorption kinetics studied under magnetic induction heating.

2. Materials and methods

2.1. Materials

The *P. janthinellum* fungus was collected from the East China Sea and stored at the China Center for Type Culture Collection (CCTCC), CCTCCM 2012006. It was initially grown on Potato Dextrose Agar (PDA) slant at 28 °C, and later stored at 4 °C. A modified Takashio growing medium was used for the preparation of mycelial pellets, which had a formulation of: glucose (10 g/L), ammonium tartrate (2 g/L), KH_2PO_4 (2 g/L), $MgSO_4.7H_2O$ (0.5 g/L) and yeast extract (2 g/L). The pH of the solution was 5.0 and 5–40 g/L Fe_3O_4 nanoparticles were added. Congo red as a model dye and Fe_3O_4 nanoparticles with size of ~20 nm were purchased from Aladdin Reagent (Shanghai) Co., Ltd. All chemicals were used as received.

2.2. Pellets preparation

Spore suspension with concentration of approximately 10^7 spores per milliliter was prepared and 1 mL spore suspension was inoculated into 100 mL culture media in 250 mL Erlenmeyer flasks, which were then stored in rotary shakers under 160 rpm, 28 °C for 72 h. The mycelial pellets were collected after cultivation, washed with tap water and freeze-dried. Totally four magnetic mycelial pellets were prepared with Fe_3O_4 nanoparticle concentrations in culture media of 5 g/L, 10 g/L, 20 g/L and 40 g/L, respectively (samples were named Fe_3O_4/5, Fe_3O_4/10, Fe_3O_4/20 and Fe_3O_4/40).

2.3. Characterization

Scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDAX) was studied with a scanning electron microscope (SIRION-100, Philips, Netherlands). Beads were first sputter-coated with gold before observation. Some pellets were cut into half to observe their inner structure. EDAX was applied with the same microscope to study the chemical elements on the surface of the pellets. The overall structure of the pellets before and after dye adsorption was also observed with a stereo-microscope. The weight percentage of the Fe_3O_4 nanoparticle in the pellets was measured with a thermo-gravimetric analyzer (TA-Q500, TA Instruments, USA) from 50 °C to 600 °C under nitrogen atmosphere with a temperature increasing rate of 10 °C/min. Approximately 3 mg samples were used for thermo-gravimetric analysis. Each measurement was repeated for three times and the data was averaged.

2.4. Magnetic induction

An alternating magnetic field generating setup (IPS200KW40KC, Sanyi electronics, China) with a 300 kHz radiofrequency generator was used. 0.1 g freeze-dried mycelial pellets were added into 20 mL Congo red solution in a flask which was settled in a water cooled copper coil of the alternating magnetic field generating setup. The Congo red liquid solution temperature was controlled by adjusting the power input, and the temperature that was controlled at 28 ± 1 °C was measured with an IR thermometer (62MAX+, Fluke, USA) and a regular mercurial thermometer.

2.5. Adsorption isotherms

0.1 g freeze-dried mycelial pellets were added into 20 mL Congo red solutions with dye concentrations of 25, 50, 100, 250, 500, 2500 and 5000 mg/L, respectively. The solutions were kept in rotary shakers at 120 rpm under 28 °C for 24 h, and the finial Congo red concentration was measured with a UV spectrometer (UV-1800, Shimadzu, Japan). The experimental results were fitted with Langmuir, Freundlich and Langmuir–Freundlich models to calculate the maximum adsorption capacities.