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Pleurotus ostreatus nanoparticles as a new nano-biosorbent for removal of Mn(II) from aqueous solution

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HIGHLIGHTS

- *Pleurotus ostreatus* was fabricated into nanoparticles by high-energy nano-impact grinding.
- *P. ostreatus* nanoparticles as a new nano-bisorbent for removal of Mn(II).
- The size distribution of PONP measured by small angle X-ray scattering.
- SEM, EDS and FTIR spectra were used to characterize the nano-biosorbent.
- The maximum Mn(II) adsorption capacity of PONP is higher than many other adsorbents.

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ABSTRACT

The objective of this study was to investigate the use of *Pleurotus ostreatus* (*P. ostreatus*) nano-particles (PONP) as a new nano-biosorbent to remove Mn(II) from aqueous solution. Scanning Electron Microscope (SEM), Energy Dispersive Spectrometry (EDS), Fourier Transform Infrared Spectrometry (FTIR spectra), Small-angle X-ray Scattering (SAXS) were used to characterize the nano-biosorbent. Adsorption experiments were carried out by batch experiments to investigate the effects of different experiment parameters including pH of the solution, adsorbent dose, initial Mn(II) ion concentration and contact time on adsorption capacity of PONP. The adsorption equilibrium study exhibited that Mn(II) adsorption of PONP was better fitted by Langmuir isotherm model. The maximum Mn(II) adsorption capacity of PONP was 130.625 mg/g at 298.15 K, which was higher than many other adsorbents. Pseudo-second-order kinetic model was the best one to predict the sorption kinetics with a maximum adsorption capacity of PONP attained within 30 min. PONP showed great potential in wastewater treatment due to the high adsorption capacity.

1. Introduction

Nanotechnology, as a novel method, has become one of the most popular technologies for the removal of metal cations from aqueous solution over the past few decades. Nano-particles mainly including nano-sized inorganic material derived from metals and metal oxides (i.e., silver nano-particles, TiO_2, SiO_2, Al_2O_3 and ZnO, Fe_3O_4 magnetic nano-particles), carbon nanotube and synthetic nano particles (i.e., synthetic nanostructured Fe(III)–Cr(III) mixed oxide [1]) have been applied widely as adsorbents for the treatment of metal cations effluents. The advantages of various types of nano-particles adsorbents are tiny in particulate diameter, large external surface area, high density of reactive surface sites and great intrinsic reactivity of surface sites and small internal diffusion resistance [2]. However, these nano-adsorbents have many obvious shortcomings such as high preparation cost, strict operational conditions, high energy consumption. These shortcomings which may restrict application areas of nano-particles adsorbents in wastewater treatment already became a serious problem cannot be ignored. Fortunately, a number of naturally available, low-cost and effective adsorbents including activated olive bagasse [3], Chitosan [4], Dehydrated peanut hull [5], Cedar sawdust [6] and some types of edible mushrooms (such as *Pleurotus platypus* [7], *Lentinus sajor-caju* [8]) have been successfully employed as adsorbents for removing various kinds of metal cations and dyes from waste water in recent years. *Pleurotus ostreatus* is a normal edible mushroom, which is extensively cultivated in South China. Because of wide source of raw materials and technological innovation, PONP combine the merits of nano-particles adsorbents and low-cost adsorbents. It retains high surface-area-to-volume ratio and low capital and operational costs.

It is worthwhile to note that adsorbent particle size has a significantly effect on water pollutants removal in previous researches.

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Investigators [9–13] found that adsorption capacity of heavy metals or dyes increased with the decrease in adsorbent particle size. Tian et al. [9] studied spent *Tricholoma lobayense* for removal of Congo Red (CR) from aqueous solution. The CR removal percentages increased from 81.27% to 92.75% when the particle size of adsorbent decreased from 60 mesh to 200 mesh. They came to the conclusion that both removal ratio of CR and adsorption capacity increased with the decrease in adsorbent particle size. Liu et al. [10] used ammonium citrate modified spent *Lentinus edodes* as adsorbent to remove Pb(II) from aqueous solution. Particle size of adsorbent was proved by Placket–Burman design that it had a positive effect on Pb(II) removal. Gupta et al. [11] studied on the removal of Cr(VI) from aqueous solution using carbon slurry and found that the adsorption capacity increased with the decreasing of particle size of the adsorbent. Chen et al. [12] applied *L. edodes* to the bioremediation of chromate contaminated water. Three sizes of the biosorbent, 2 mm, 1 mm and 450 μm, were used in 100 mg/L Cr(VI) for adsorption. Total removal of Cr(VI) achieved was the highest at 450 μm among these three sizes.

Albadarin et al. [13] removed chromium ions from aqueous solution using raw dolomite. Experiments were performed using different particle sizes of the adsorbent (0.180–2.0 mm). Results specified that the amount of Cr(VI) adsorbed onto dolomite decreases with an increase in the particle size of the adsorbent. These results of such studies can demonstrate that the adsorption capacity of adsorbent particle may be enhanced by reducing the size of particle. But very few literatures are available on metal ions removal using nanoparticles biosorbent.

Toxic metals contamination of the environment such as copper, lead, cadmium, nickel, mercury, manganese is a severe global environmental issues. It has long been known that Mn is one of the most widely used metals in the world and one of the important indexes of the water pollutants. As an essential element for humans, animals and plants, Mn is required for their growth, development, and maintenance of health. But excess manganese is detrimental to health. In China, the maximum recommended level of Mn(II) in drinking water is 0.1 mg/L as well as the provisions of World Health Organization. Overdose exposure to Mn(II) in the environment may result in the occurrence of manganese poisoning, which can adversely affect human body system such as nervous system, immune system and reproductive system. Chronic inhalation of high levels of Mn can induce a neurodegenerative disorder, Parkinson, lung embolism and bronchitis [14].

To our knowledge, no similar report about nano-size mushroom applied to waste water treatment is available up to now. Furthermore, our study was the first one in which *P. ostreatus* was fabricated into nanoparticles by high-energy nano-impact grinding (HENIG). HENIG as a closed high-energy milling machine and through the quick multidimensional swing motion of its tank, is able to make the irregular motion of milling medium in the tank. The motion can generate a tremendous impact force with increased impact times, prolong the motion trace, augment the impact energy and lessen the impact blind spots. Its working efficiency increased several dozen times over the traditional ball millers. The particles of broken substance processed by HENIG reach nano-grade. Because HENIG are high-energy millers, mushroom fines are easy to be cooked and carbonized in the quickly increasing temperature in the machines. To solve the problem, cycling water cooling in a jacket of the tank are adopted to effectively control the temperature during the processing. Numerous kinds of mushroom contain too much sugar or oil or colloid that might stick onto the balls and the tank or palletized in the ball miller, which reduce the milling effect. The humid milling method have solved the problem of stickiness. To improve milling effect, mushroom are crashed and water is added to form specified size, and then made with ball miller into nano-size, finally dried with spray after having reached milling effect.

First, material crushed with traditional method, second, crushed with air flow, finally, the micro-grade materials are prepared into nano-fines with high-energy ball milling. From the above steps, machining time are shortened and decreased the pollution. Controlled in the first two steps (crush, screen, crush with air flow and screen again), the evenness can be achieved as expected.

Therefore, the main objective of this study was to investigate the potential of the nanoparticles biosorbent as low-cost adsorbent in the removal of the Mn(II) from aqueous solutions. In this research, PONP prepared by HENIG was characterized and used as an adsorbent to remove Mn(II) from aqueous solution. The adsorption of Mn(II) ions onto PONP was studied in batch equilibrium experiments conditions. The work investigates the effect of different parameters including pH, initial Mn(II) concentration, adsorbent dose on Mn(II) adsorption. Adsorption isotherms and kinetics models were conducted to describe the experimental data and understand the adsorption mechanism.

2. Materials and methods

2.1. Reagents and adsorbate

All chemical reagent of analytical grade were purchased from Kelong Chemical Reagent Factory, Cheng du, Sichuan province, China. Deionized water was always used in the experiments. A stock aqueous solution of Mn(II) of 1000 mg/L was prepared by dissolving 3.6024 g manganese chloride tetrahydrate ($MnCl_2\cdot4H_2O$) in 1 L deionized water. $MnCl_2\cdot4H_2O$ with purity 99.99% has a molecular weight of 197.91 g/mol. Diluting the stock solution to get the required concentration of the Mn(II). Before adding adsorbent, pH of Mn(II) solution were adjusted to desired values by adding volume-negligible HNO_3 (0.01 M, 0.1 M, 1 M) or NaOH (0.01 M, 0.1 M, 1 M). The pH value was measured by a pH meter (Model pHS-25, calibrated with buffers of pH 4.00, 6.86 and 9.18). The concentration of Mn(II) ion in solutions was analyzed by flame Atomic Absorption Spectrometer (AAS; VARIAN, SpectrAA-220Fs).

2.2. Preparation and characterization of nano-biosorbent

Fresh *P. ostreatus* which was obtained from a mushroom production base in the suburbs of Chengdu, Sichuan Province, China, was washed with deionized water and later dried in an oven at 328.15 K. Then the dried *P. ostreatus* grounded into powder using a pulverizing mill (Joyoung, JYL-350B) to obtain raw biomass for further use. The dried *P. ostreatus* particle were dropped into the HENIG (Taijihuan, CJM-SY-A) with 373.15 K drying 2 h and 10 h of continuous milling. The small particles reach to a certain extent will trigger oxidation which is caused by increased surface areas, and then the phenomena of explosion will emerge. So nitrogen was added to reaction vessels when the material in the process of grinding to prevent oxidation and spontaneous combustion. The FTIR spectra analysis of the nano-biosorbent used in this study was characterized with a FTIR (NEXUS-650, America).

In order to directly observe the surface morphology of the nano-biosorbent, SEM (JSM-5900LV, Japan) was employed in this study. For analyzing the elemental constitute of metal-free and metal-loaded of PONP, as well as further confirming the identity of metal ions onto PONP, EDS (JSM-5900LV, Japan) was used. The size distribution of PONP measured by small angle X-ray scattering (SAXS) (MAX-2500, Japan).

2.3. Batch adsorption studies

To study important factors, all the experiments were performed in 150 ml conical flasks containing 50 ml solution in each flask at