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Application of bifunctional Saccharomyces cerevisiae to remove lead(II) and cadmium(II) in aqueous solution

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ABSTRACT

A magnetic adsorbent, EDTAD-functionalized Saccharomyces cerevisiae, has been synthesized to behave as an adsorbent for heavy metal ions by adjusting the pH value of the aqueous solution to make carboxyl and amino groups protonic or non-protonic. The bifunctional Saccharomyces cerevisiae (EMS) were used to remove lead(II) and cadmium(II) in solution in a batch system. The results showed that the adsorption capacity of the EMS for the heavy metal ions increased with increasing solution pH, and the maximum adsorption capacity (88.16 mg/g for Pb^{2+}, 40.72 mg/g for Cd^{2+}) at 10 °C was found to occur at pH 5.5 and 6.0, respectively. The adsorption process followed the Langmuir isotherm model. The regeneration experiments revealed that the EMS could be successfully reused.

1. Introduction

Water pollution is one of the most serious environmental problems facing modern society [1,2]. Heavy metals cause a series of serious environmental problem because these substances are not biodegradable and are highly toxic to living organisms [3,4]. Toxic metals such as Pb^{2+}, Cd^{2+} and Ni^{2+} have become an ecotoxicological hazard of prime interest and increasing significance owing to their tendency to accumulate in the vital organs of humans and animals [3,4]. The commonly used processes for removing heavy metal ions from waste water include chemical precipitation and filtration, chemical oxidation or reduction, electrochemical treatment, reverse osmosis, ion exchange, evaporation and adsorption, etc. [1,2]. However, these conventional processes were sometimes restricted by the technique and/or economy. Research in recent years indicates biosorption is one of the most promising technologies, which can remove heavy metals from even very dilute aqueous solutions [5,6]. There are many reports on microorganisms which can remove and/or accumulate large amounts of heavy metals from their external environment [7,8].

Saccharomyces cerevisiae biomass is one of the most common microorganisms available in large quantities which are the byproduct of the fermentation or pharmaceutical industry processes. Investigations conducted by several researchers demonstrated that Saccharomyces cerevisiae could be utilized as a biosorbent to remove or accumulate heavy metals, such as Cu^{2+}, Cd^{2+}, Pb^{2+} and Hg^{2+}, etc., from waste water [3,9]. However, it is well known that for Saccharomyces cerevisiae, there are insufficient binding sites or functional groups for adsorbing metal ions, which usually leads to the poor adsorption capacity, and difficult regeneration in a practical application, which will directly cause the cost increasing.

Magnetic separation technique has been shown to be a very promising method for solid–liquid phase separation [10–12]. Nano-Fe_3O_4, which is super-paramagnetic, has been used in many fields [13–16]. To facilitate the regeneration and recovery of Saccharomyces cerevisiae, nano-Fe_3O_4 is cross-linked/incorporated with the Saccharomyces cerevisiae. This will make magnetic Saccharomyces cerevisiae (MS) a wonderful candidate for combining adsorption properties with ease of phase separation.

Ethylenediaminetetraacetic dianhydride (EDTAD) is a biodegradable and active agent containing two anhydride groups per molecule that can be used to introduce chelating abilities to the biomaterials through esterification/amidation reaction [17–19]. This reaction allows introducing carboxylic and amine functional groups which present high ability to form stable complexes with heavy metal ions and thus EDTAD-functionalized Saccharomyces cerevisiae will possess good chelating ability for heavy metal ions.

In this study, the main objective of this work was to explore the possibility to produce bifunctional Saccharomyces cerevisiae (EMS) with exploitable characteristics as an adsorbent for Pb^{2+}/Cd^{2+}

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removal from aqueous solution. To our knowledge, the relationship between the adsorption capacity of Pb^{2+}/Cd^{2+} and the amount of functional groups introduced to Saccharomyces cerevisiae's surface and the conditional stability constant of metal complex is first proposed. Moreover, the EMS was characterized by SEM, FTIR, XRD, potentiometric titration, and Zeta potential analysis. The removal process has also been investigated at different experimental conditions of time, pH, temperature, and initial concentrations of adsorbate. The mechanism of interaction between the functional groups on the EMS and metal ions as well as regeneration properties of EMS will also be clarified.

2. Experimental

2.1. Materials and reagents

The fresh commercial Saccharomyces cerevisiae, supplied by Harbin Mali Ltd. China, was washed with ultra pure water several times till it reached pH 7. This means that the nutritional ions and the edible fixation glue were removed. The resulting biomass was centrifuged at 4000 rpm and was collected. The wet Saccharomyces cerevisiae was dried at 80 °C for 24 h and then ground to granular material with geometrical particle sizes of 100–120 mm mesh. Finally, the yeast was stored in a desiccator.

Stock standard solution of $Cd(NO_3)_2/Pb(NO_3)_2$ with 1000 μg/mL Pb^{2+}/Cd^{2+} was obtained from the National Analysis Center for iron and steel (Beijing, China). The working solutions were diluted from the above stock solution. Other reagents obtained from KeLong Corp., China, were analytical grade. Ultra-purity water with a resistivity of 18.23 MΩ cm^{-1} obtained from a pure water system (Ai Kuo, KL-UP-II-20, China) was used throughout the experiment.

2.2. Preparation of magnetic Saccharomyces cerevisiae (MS)

The synthetic strategy of nano-Fe_3O_4 was preformed according to Shan's method [12]. After the prepared nano-Fe_3O_4 (1.0 g) was dispersed in 200 mL of ultra pure water by ultrasonic, the Saccharomyces cerevisiae (5.0 g) and glutaraldehyde solutions (100 mL, 1.5 wt% in water) were added into the suspension. After the mixture was shaken at room temperature for 24 h on a rotary shaker (DH2-DA China), the magnetic biomass (MS) was magnetically separated and washed several times. The MS was freeze-dried in a high vacuum for 24 h and preserved in a desiccator.

2.3. Preparation of bifunctional Saccharomyces cerevisia (EMS)

EDTA dianhydride (EDTAD) was prepared following the methodology described before [17]. The prepared EDTAD (2.0 g) was added to 100 mL of N,N-dimethylformamide (DMF) containing 5.0 g of MS in a three neck round bottom flask equipped with a condenser. After the mixture was stirred at 60 °C for 4 h, the EMS was magnetically separated and washed with DMF (200 mL), ultra-purity water (500 mL), and 10% $NaHCO_3$ solution (100 mL), successively. Then the EMS was freeze-dried in a high vacuum for 24 h and preserved in a desiccator.

2.4. Characterization of EMS

The iron content in EMS and MS was measured by an atomic absorption spectrometer (Shimadzu AA-6300, Japan), respectively. The XRD pattern of nano-Fe_3O_4 and EMS were obtained by a diffractometer (Holland Philip-X'Pert Pro) with Cu Kα radiation (λ = 0.15406 nm) in steps of 0.03° (2θ) min^{-1} from 15° to 75° (2θ). The surface structure and morphology of EMS, MS and nano-Fe_3O_4 were characterized using a scanning electron microscope (JEOL JSM-5900LV, Japan) at a 20 kV acceleration voltage. Prior to SEM analysis, the samples were coated with a thin layer of gold. The zeta potential of MS and EMS was measured using zeta potential analyzer (Malvern-Zetasizer nano ZS UK) at different pHs. The type of binding groups present on the EMS and MS were identified by Fourier transform infrared spectroscopy (Shimadzu FTIR-8400S, Japan) analysis in the region of 400–4000 cm^{-1} via the KBr pressed-disc method. The active sites present on the surface of MS and EMS were determined by potentiometric titration on autotitrator (ZD-2, China) with a combined glass electrode. The software ProtoFit Version 2.0 [20–24], a useful software tool for the calculation of pK_a values as well as surface site densities of biological material, was employed to fit the acid–base titration data of MS and EMS.

2.5. Metal adsorption studies

Adsorption experiments were carried out in 250 mL glass-stoppered conical flasks agitated at 200 rpm in a rotary shaker (DH2-DA, China). For this, 0.1 g of dry sample was mixed with 100 mL of metal ion (Cd^{2+} and Pb^{2+}) solution at a known initial concentration. The flasks with their contents were shaken for different time intervals at various temperatures and pHs. The initial pHs of the solutions (2–6) were adjusted with 0.1 mol/L HCl or 0.1 mol/L NaOH solutions. At the end of the adsorption period, the supernatant was magnetically separated by an external magnetic field. The concentration of metal ion (Cd^{2+} and Pb^{2+}) in the supernatant solution before and after the adsorption was determined by an atomic absorption spectrometer (Japan ShimadzuAA-6300). The adsorption capacity was calculated using the following relationships:

$$q_t = \frac{(C_i - C_t)V}{m} \quad (1)$$

where q_t is the amount of adsorption capacity at time t (mg/g), C_i is the initial concentration of metal ions (mg/L), C_t is the metal ions concentration at time t (mg/L), V is the volume of the solution (L), and m is the mass of the adsorbent (g).

2.6. Effect of coexisting ions

The uptake behaviors of Pb^{2+}/Cd^{2+} from binary mixtures with 200 mg/L coexisting cation nitrates, such as Ni^{2+}, Cu^{2+}, Ca^{2+}, Mg^{2+} and Na^{+} ions, were studied at pH 5. The procedures were the same those of Section 2.5.

2.7. Regeneration studies

In order to determine the reusability of the EMS, the heavy ions-loaded EMS, which were harvested by magnetic separation from the EMS/metal solutions (200 mg/L for Pb^{2+} at pH 5.5, 300 mg/L for Cd^{2+} at pH 6) at 10 °C after adsorption experiments, were rinsed three times with ultra pure water to remove the physically attached metal ions. Afterwards, the washed EMS was added to 100 mL of HCl (0.1 mol/L). Later, the mixture shaken for 30 min was magnetically separated. The metal desorption efficiency of Pb^{2+}/Cd^{2+} was calculated by the following expression:

$$\text{Metal desorbed efficiency} = \frac{\text{Amount of metal ions desorbed}}{\text{Amount of metal ions adsorbed}} \times 100\% \quad (2)$$

3. Results and discussion

3.1. The experimental procedure

The preparation route used to prepare EMS and the possible mechanism involved in Pb^{2+}/Cd^{2+} removal are shown in Fig. 1.