Chemical Engineering Journal 168 (2011) 737–745

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Study on the adsorption of Ca^{2+}, Cd^{2+} and Pb^{2+} by magnetic Fe_3O_4 yeast treated with EDTA dianhydride

Meng Xu[a,1], Yunsong Zhang[a,1], Zhiming Zhang[b], Yaou Shen[b], Maojun Zhao[a,*], Guangtang Pan[b,*]

[a] College of Life and Science, Sichuan Agricultural University, Yaan 625014, PR China
[b] Maize Research Institute, Sichuan Agricultural University, Yaan 625014, PR China

ARTICLE INFO

Article history:
Received 18 November 2010
Received in revised form 17 January 2011
Accepted 17 January 2011

Keywords:
Baker's yeast
Nano-Fe_3O_4
Super-paramagnetic
EDTAD
Chemically treated
Adsorption

ABSTRACT

Magnetic Fe_3O_4 baker's yeast biomass (FB) was prepared by combining baker's yeast biomass and nano-Fe_3O_4 using glutaraldehyde as a cross-link agent, and was chemically treated with ethylenediaminetetraacetic dianhydride (EDTAD). The EDTAD-treated magnetic Fe_3O_4 baker's yeast biomass (EFB) was investigated by Fourier transform infrared spectroscopy (FTIR), potentiometric titration, zeta potential, and magnetic response analysis. The results revealed that the EFB possessed not only the super-paramagnetic characteristic of nano-Fe_3O_4, but its surface also had plenty of carboxyl and amino groups introduced by the EDTA molecules. The adsorption properties of EFB for Pb^{2+}, Cd^{2+}, and Ca^{2+} ions were also evaluated. The results showed that the uptakes of EFB for the three metal ions were higher than that of FB, and the adsorption capability of Pb^{2+}, Cd^{2+}, and Ca^{2+} ions increased with an increase in pH. The adsorption process was followed by the pseudo-second-order kinetic model and Langmuir isotherm equation. The maximum adsorption capacities of 99.26 mg/g for Pb^{2+} at pH 5.5, 48.70 mg/g for Cd^{2+} at pH 6.0, and 33.46 mg/g for Ca^{2+} at pH 6.0 were observed at 30 °C. The regeneration experiments showed that the EFB could be successfully reused.

1. Introduction

Water pollution, especially heavy metal ion pollution, is currently one of the most serious environmental problems [1,2]. Heavy metal ions such as lead, copper, cadmium, zinc, nickel, and others are the most common pollutants found in industrial effluents [3]. They are non-biodegradable, and thus some heavy metal ions, even at low concentrations, are highly toxic to living organisms [4]. Among them, lead and cadmium can directly damage the nervous, reproductive, and skeletal systems and the kidney, and can even cause cancer. Thus, finding an efficient method that can purify waste water is necessary. Although there are traditional methods, such as chemical precipitation, ion exchange, electrolysis, filtration, extraction, and evaporation, among others [5–8], these are sometimes restricted by practical technique or economic factors [9].

Recently, the utilization of biomass and agricultural waste materials for the removal of metal ions has been explored [10–12]. Attention has been diverted toward the usage of biomaterials, which are byproducts or wastes from large-scale industrial and agricultural production [13,14]. *Saccharomyces cerevisiae*, which has been considered a cheap, available, and safe industrial microorganism, is an economic and constant supply source of microorganism for the removal of heavy metal ions [15,16]. Investigations conducted by many researchers have demonstrated that baker's yeast biomass is capable of accumulating heavy metals, such as Cu^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}, and others from waste water [7]. However, because the adsorption capability of heavy metal ions by waste brewery biomass is lower, improving the removal efficiency of the yeast biomass by chemical treatment methods becomes the focal point in recent research [9,17].

Ethylenediaminetetraacetic acid (EDTA), a powerful complexing agent, is widely commercially available. EDTA, which is a Lewis acid, has six binding sites, four carboxyl and two amino groups, providing six pairs of electrons. The resulting metal–ligand complex, where EDTA forms a cage-like structure around the metal ions, is very stable. EDTA dianhydride (EDTAD), a ramification of EDTA containing two anhydride groups per molecule, can react with hydroxyl and amino groups of other materials. The use of EDTAD to treat baker's yeast biomass for producing biosorbents with high adsorption capacity of Pb^{2+} and Cu^{2+} ions has been reported in the study [18]. However, the separation of EDTAD-treated baker's yeast biomass from disposed waste water, as well as the regeneration of the adsorbents, is very difficult in practical application.

* Corresponding authors. Tel.: +86 835 2885782; fax: +86 835 2862227.
E-mail address: numberlala123@163.com (M. Zhao).
[1] These authors contributed equally to this work.

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doi:10.1016/j.cej.2011.01.069

Nanomaterials are widely considered as the new functional materials; they have been utilized in various fields such as medicine, environment, and industry [19,20]. Nano-Fe_3O_4, which is superparamagnetic, presents high recovery ability [21]. To facilitate the recovery of baker's yeast, Fe_3O_4 nano-particles are loaded on the baker's yeast biomass, enabling it as an efficient candidate for combining adsorption properties with ease of phase separation in the removal of heavy metal ions.

In this work, the magnetic Fe_3O_4 baker's yeast biomass (FB) was prepared using glutaraldehyde as a cross-link agent and was chemically treated with EDTAD. The resulting EDTAD-treated FB (EFB) was investigated by magnetic response, Fourier transform infrared (FTIR) spectroscopy, potentiometric titration, and zeta potential analysis. The mechanisms of EFB were studied. EFB was utilized as an adsorbent for the removal of Ca^{2+}, Cd^{2+}, and Pb^{2+} in the solution. The effects of the experimental parameters such as time, pH, temperature, and initial concentration of the adsorbate on adsorption were also investigated. The mechanism of interaction between the functional groups on EFB and metal ions as well as the regeneration properties of EFB was also clarified.

2. Materials and methods

2.1. Materials

Baker's yeast was purchased from Harbin Mali Ltd., China. The samples were repeatedly washed with deionized water to remove dirt and soluble impurities. They were dried at 80 °C for 24 h. Afterwards, they were crushed and sieved to a particle size of under 100 meshes using a standard sieve.

The stock standard solution of $Cd(NO_3)_2$, $Pb(NO_3)_2$, and $Ca(NO_3)_2$ with 1000 μg/mL Pb^{2+}, Cd^{2+}, and Ca^{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 chemicals were of analytical grade and were purchased from ChengDu KeLong Corp., China. Ultrapure water with resistivity of 18.23 MΩ/cm obtained from a pure water system (Ai Kuo, KL-UP-11-20) was used throughout the experiment.

2.2. Synthesis of EFB

2.2.1. Preparation of FB

The synthetic nano-Fe_3O_4 was prepared according to Shan Zhi's method [22]. NaOH at 4 mol/L (100 mL) was placed in a three-neck flask under nitrogen flow at 150 rpm stirring at 65 °C for 30 min; 56 mL of solution containing Fe_2SO_4 (0.01 mol) and $FeCl_3$ (0.018 mol) was quickly added. The resultant mixture was stirred for 90 min and was washed with ultrapure water until the pH of the supernatant became neutral with the help of an external magnetic separator. The resultant dark precipitate was placed in a vacuum drying oven overnight until further use.

After 1.0 g of synthetic nano-Fe_3O_4 was dispersed in 200 mL of ultrapure water by ultrasonication for 20 min, 5.0 g of dry baker's yeast biomass and 100 mL glutaraldehyde solutions (1.5 wt% in water) were added to the suspension; the mixture was stirred at room temperature for 24 h. After the reaction, FB was obtained by an external magnet and was washed thrice before it was freeze-dried in high vacuum for 24 h. Finally, FB was preserved in a desiccator for further use.

2.2.2. Synthesis of EDTAD

EDTAD was prepared following the methodology described by Capretta et al. [23]. About 18.0 g EDTA was suspended in 30 mL anhydrous pyridine. Then, 24 mL of acetic anhydride was added to the suspension. The mixture was stirred at 65 °C for 24 h. EDTAD obtained was filtered. It was then washed with acetic anhydride and diethyl ether before it was dried under vacuum and stored in a desiccator.

2.2.3. EDTAD treatment of FB

Approximately 2.0 g of EDTAD was added to 100 mL of *N*,*N*-dimethylformamide (DMF) containing 5.0 g of FB in a three-neck round bottom flask equipped with a condenser. The mixture was stirred at 60 °C for 4 h. After the reaction, EFB was isolated from the mixture by an external magnet and then washed with DMF, ultrapure water, and 10% $NaHCO_3$ solution, respectively. EFB was freeze-dried in high vacuum for 24 h and then preserved in a desiccator for further use.

2.3. Biosorption studies

Batch biosorption studies were conducted in 100 mL conical flasks at different temperatures (10, 20, 30, 40, 50, and 60 °C). Then, 100.0 mL of metal ion (Cd^{2+}, Ca^{2+}, and Pb^{2+}) solution at an initial concentration of 40–300 mg/L was stirred at 150 rpm in a rotary shaker (DH2-DA, China) with 0.1 g dry sample for a required biosorption time (5–120 min). Varying pH values of the solutions (2–6) were used. Afterwards, the external magnetic field was applied to separate the samples from the solution. The supernatants were analyzed to determine the concentration of the metal ions by an atomic absorption spectrometer (Japan Shimadzu AA-6300). The adsorption capacity was calculated using the following relationships:

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

$$Q\,(\%) = \frac{C_i - C_t}{C_i} \times 100\% \quad (2)$$

where q_t is the amount of adsorption capacity at time t (mg/g), Q is the metal ions uptake efficiency, 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).

2.4. Desorption studies

Desorption studies were carried out in 100 mL conical flasks. The metal ion-loaded EFB was magnetically separated. The settled EFB was eluted with different eluents. The suspension was shaken at 150 rpm for 30 min to release the metal ions from the EFB. The desorbed metal ions were analyzed, and the metal ions recovery efficiency was calculated. The EFB regeneration efficiency was calculated as follows:

$$\text{Metal desorbed efficiency} = \frac{\text{Amount of metal ions desorbed}}{\text{Amount of metal ions adsorbed}} \times 100\% \quad (3)$$

2.5. Characterization of EFB and FB

The zeta potential of EFB and FB (with/without metal ions) was measured using a zeta potential analyzer (Malvern–Zetasizer nano ZS, UK) at pH 5. The types of binding groups present in the EFB and FB were identified by FTIR spectroscopy (Shimadzu FTIR-8400S, Japan) analysis in the region of 400–4000 cm^{-1} through the KBr pressed-disc method. The active sites present on the surface of EFB and FB were determined by the potentiometric titration on an autotitrator (ZD-2, China) with a combined glass electrode. The software ProtoFit Version 2.0 [24,25], a useful software for the calculation of pK_a values and functional groups on the surface of biological material, was employed to fit the acid–base titration data of the FB and EFB.