Chemical Engineering Journal 214 (2013) 189–197

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

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

Removal of lead(II) from aqueous solution with ethylenediamine-modified yeast biomass coated with magnetic chitosan microparticles: Kinetic and equilibrium modeling

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HIGHLIGHTS

- ▸ The EYMC is an excellent adsorbent for the removal of Pb(II) ions.
- ▸ The EYMC can be separated from reaction medium easily.
- ▸ The experiment data fitted best with Langmuir and pseudo-second-order models.
- ▸ The adsorption showed a spontaneous and endothermic adsorption process.
- ▸ EYMC was regenerated successfully and only lost 0.61 mg g^{-1} after four cycles.

ARTICLE INFO

Article history:
Received 11 August 2012
Received in revised form 28 October 2012
Accepted 29 October 2012
Available online 7 November 2012

Keywords:
Biosorption
Lead(II)
Kinetic
Equilibrium isotherm

ABSTRACT

The adsorption of Pb(II) ions from aqueous solution with ethylenediamine-modified yeast biomass coated with magnetic chitosan microparticles (EYMC) was studied in batch adsorption system. The adsorption of Pb(II) ions increased with the rising pH and a higher adsorption capacity was achieved at the pH 4.0–6.0. The experiment data was well matched by Langmuir model and Freundlich model, while Langmuir model showed the best description. The maximum adsorption capacities obtained by Langmuir model were 121.26, 127.37 and 134.90 mg g^{-1} at 20, 30 and 40 °C, respectively. Kinetic studies indicated that the pseudo-second-order model was appropriate to describe the adsorption process and film diffusion maybe governed the rate of the adsorption. Thermodynamic studies revealed that a spontaneous and endothermic adsorption process. The adsorbents, EYMC can be well recovered by 0.1 M EDTA.

1. Introduction

The release of lead has recently attracted great attention because of its widespread adoption, toxic effects, accumulation in living tissues and adverse impact on human health [1]. Therefore, disposal of metal ions from source water is necessary before discharging into the environment. Innovative and improved methods have developed to remove metal ions from metal-laden wastewater, such as chemical precipitation, ion exchange, electrolysis, coagulation, membrane separation, reverse osmosis processes, and adsorption [2]. However, great challenges are faced by these methods due to the technological problems, ineffectiveness at low metal concentration and high cost [3]. Biosorption is considered as one of the promising technologies and has been continuously studied in recent years. A variety of living and dead microorganisms or biomaterials, such as bacteria, fungi, algae, yeast, and mosses have been proved their credibility in dilute metal ions [4–6]. Since no growth media or nutrients are required, the use of dead cells has more advantages than living cells. Moreover, dead cells have lower sensitivity to the pollutant concentration and an easy mathematical modeling [7]. In the practical application of industrial operation, immobilization is regarded as an effective method to improve the applicability of the adsorbents. This technique provides the superiorities of improved mechanical strength, good performance, rigidity and porosity characteristics to the

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1385-8947/$ - see front matter
http://dx.doi.org/10.1016/j.cej.2012.10.055

adsorbents [8]. Moreover, the processes of adsorption are more competitive and economic for their easy operation of repeating adsorption–desorption cycles [9].

The choice of adsorbent is not only determined by their sorption capability, kinetic parameters but also by their price and reusability. The overall economic is mainly influenced during the choice of experimental biomass [10]. Yeast is widely used in the field of fermentation, bread production and xylitol production. According to the various studies yeast biomass can chelate copper, lead, cadmium, mercury and methyl violet to the amino and hydroxyl groups of the biomass surface [11,12]. The enhancement of the biosorption capacity is presently practicable by several techniques, including the heat treatment, freeze drying, acids, alkalis, and organic chemicals [13,14]. The biosorption capacity was efficiently improved by the selective modification of *Rhizopus niqricans* [15]. Moreover, according to Volesky et al. [13] the removal of cadmium from metal-laden water is currently feasible thanks to dried yeast.

A quantity of synthetic polymers was used in order to immobilize microbe. The choice of chitosan is due to its reactive groups (amino and acetamido), excellent ability to chelate resins, high hydrophilicity, biodegradability and ease of chemical derivatization. In addition, chitosan has been proved environmental friendly [16]. Nevertheless, chitosan solubility at low pH is poor. In order to improve the stability in acid solutions, many cross-linking agents such as glutaraldehyde, glyoxal, and epichlorohydrin were used [16,17].

Traditional methods of separation after adsorption are filtration, sedimentation and centrifugation. Yet they may inefficient and uneconomical. The problem is easily resolved by magnetic materials. Magnetic carriers serve as supporting materials for adsorbents and they are easily separated from the aqueous solutions by an external magnet [18].

The ability of eliminating metal ions from solutions is influenced by the number of available reactive groups on the material surface. In order to increase the adsorption capability, various chitosan derivatives, such as glycine, polydimethylsiloxane, and thioureaandmaleic anhydride are used [17,19].

This work focused on the sorption of Pb(II) by ethylenediamine-modified yeast biomass coated with magnetic chitosan microparticles (EYMC). Variable effects including initial pH, temperature, initial Pb(II) concentration, contact time and desorption properties were considered. In order to investigate the mechanism of the sorption, the collected experiment data was fitted to kinetic and equilibrium models. In order to compare the capability of the sorbents, the other three sorbents (yeast biomass coated with magnetic chitosan microparticles (YMC), ethylenediamine-modified magnetic chitosan microparticles (EMC) and magnetic chitosan microparticles (MC) were prepared and used as the control group.

2. Materials and methods

2.1. Materials

Chitosan (90% acetylation degree) was supplied by Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. Glutaraldehyde and epichlorohydrin were provided by Tianjin Guangfu Fine Chemical Research Institute, Tianjin, China. Ethylenediamine was obtained from Changsha Subintersection Plastic Chemical Factory, Changsha, China. Ferric chloride-6-hydrate and ferrous chloride-4-hydrate were purchased from Tianjin Kermel Reagent Co. Ltd., Tianjin, China. The yeast was purchased from Hunan Normal University. Stock solutions of lead(II) were prepared by dissolving $Pb(NO_3)_2$, obtained by Sanpu Chemical Reagent Co. Ltd., Shanghai, China. All the reagents were of analytical grade. Distilled water was provided from a distilled water system, purchased from Shanghai Boxun Co. Ltd., China.

2.2. Preparation of magnetic fluid

Magnetic fluid was prepared according to the method reported by Bao et al. [20]. Under the protection of N_2, $FeCl_2{\cdot}4H_2O$ and $FeCl_3{\cdot}6H_2O$ (molar ratio 1:2) were dissolved in water, then the resulting solution was precipitated by adding NaOH.

2.3. Preparation of EYMC and control group

EYMC was prepared by the following steps: first, adding the yeast suspension into the chitosan solution (1% w/v) and stirring at 30 °C for 12 h. Chitosan solution (1% w/v) was prepared by dissolving 1.0 g chitosan in 100 mL of 1% (v/v) acetic acid. Second, magnetic fluid was then injected into the reaction system and transferred into the boiling flask-3-neck. Third, 10 mL glutaraldehyde (4% v/v) was added into the system to form the particles after ultrasonic dispersion. Fourth, 12 mL ethylenediamine (purity 99%) was introduced into the mixture to modify active groups to the particles. Then the EYMC was collected by an external magnet. The resultant precipitate was finally dried by placing them in the Vacuum freeze dryer.

The synthetic method of MC, EMC and YMC was similar to the preparation of EYMC. In the whole process, EMC was produced with the absence of yeast suspension. If the synthetic process just included the first three steps, with the addition of yeast suspension, the particle was YMC; while without it, the product was MC.

2.4. Characteristic analysis

The characteristic of EYMC before and after adsorption was analyzed by the following techniques. The surface morphology of EYMC was observed by Hitachi TM 3000. The FTIR spectrum was taken by the usage of Varian 3100 FT-IR with a background spectrum measured on pure KBr. Surface area was determined by N_2 adsorption–desorption isotherm using Beckman Coulter SA3100. The Pb(II) concentration was measured at the radiation of lead atoms of 283.8 nm by Atomic adsorption spectrometer (PerkinElmer AA700, detection limit for lead is 0.03 mg L^{-1}).

2.5. Batch adsorption and desorption experiments

Batch experiments were carried out with adsorbents in a 100 mL Erlenmeyer flask containing 25 mL Pb(II) solutions on a shaker at 150 r min^{-1}. For each treatment, 25 mg adsorbent was added and agitated for an appropriate period. The concentrations of Pb(II) were determined by the Atomic adsorption spectrometer.

Four kinds of adsorbents (EYMC, MC, EMC, and YMC) were used to study the pH and temperature effect on Pb(II) ions adsorption, while the last three were used as control group. Effects of pH (2.0–6.5) experiments were studied in 25 mL Pb(II) solutions with the initial concentration of 50 mg L^{-1} at a temperature of 30 °C. Effect of temperature was investigated at the initial concentration of 50 mg L^{-1} with different temperatures of 20, 30, 40 °C, respectively. The pH was initially adjusted by 1 mol L^{-1} NaOH and HCl and not controlled during the experimentation.

Isotherm studies were carried out with different initial Pb(II) concentrations (at the range of 10–500 mg L^{-1}) by contacting 25 mg EYMC for 1 h. The experiments were conducted at different temperatures of 20, 30 and 40 °C, respectively. The amount of Pb(II) ions bounded by the adsorbent was calculated according to the following equation: