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Dynamic biosorption of Zn(II) and Cu(II) using pretreated *Rosa gruss an teplitz* (red rose) distillation sludge

Haq Nawaz Bhatti[a,*], Rabia Khalid[a], Muhammad Asif Hanif[a,b]

[a] Industrial Biotechnology Laboratory, Department of Chemistry & Biochemistry, University of Agriculture, Faisalabad 38040, Pakistan
[b] Rose Laboratory, Institute of Horticultural Sciences, University of Agriculture, Faisalabad 38040, Pakistan

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ABSTRACT

This work presented conditions for Cu(II) and Zn(II) removal using native, physically and chemically pretreated *Rosa gruss an teplitz* (red rose) distillation sludge. Cu(II) and Zn(II) sorption was found dependent on solution pH, biosorbent dose, biosorbent particle size, shaking speed, temperature, initial concentration of metal ions being sorbed and contact time. Physical and chemical pretreatments of biomass resulted in an increase or decrease in metals uptake capacity. The effect of different pretreatments is discussed in detail. Highest Cu(II) and Zn(II) biosorption capacities were observed for PEI + gluteraldehyde (68.64 mg/g) and NaOH (43.4 mg/g) pretreated biomass, respectively. The native biomass showed Cu(II) biosorption capacity that was adequately described by Freundlich isotherm, whereas Zn(II) biosorption phenomenon was described by Langmuir isotherm. The suitability of a pseudo-first-order chemical reaction for sorption of Cu(II) and Zn(II) ions onto this biomass was apparent as this kinetic model described adequately the largest part of the process.

1. Introduction

The majority of toxic metal pollutants are waste products of industrial and metallurgical processes. Their concentrations have to be reduced to meet ever increasing legislative standards. According to the World Health Organization (WHO), Zn(II) and Cu(II) are among the metals of most immediate concern. The effluents from metal finishing processes may contain up to 10 mg/L heavy metals [1]. Cu(II) is mainly employed in electric goods industry and brass production. High levels of Cu can cause toxic effects like all other heavy metals although Cu(II) is an essential trace element. Cu(II) may be found as a contaminant in food, especially shellfish, liver, mushrooms, nuts and chocolate. The presence of Cu(II) ions cause serious toxicological concerns, it is usually known to deposit in brain, skins, liver, pancreas and myocardium. According to Environmental Protection Agency (EPA) the concentration of Cu(II)) in drinking water should not exceed 1.3 mg/L [2]. Zn(II) may be found in wastewater discharges from acid mine drainage (AMD), galvanizing plants, as a leachate from galvanized structures, natural ores, and from municipal wastewater treatment plant discharges [1]. According to WHO more than 3 mg/L of zinc in drinking water is unacceptable. Too much intake of Zn(II) can lead to respiratory incapacitation, as indicated by increased respiratory activity such as breathing rate, volume and frequency of ventilation, coughing, decrease in oxygen uptake efficiency [3].

Conventional methods for removing metals from aqueous solutions include chemical precipitation, chemical oxidation or reduction, ion exchange, filtration, electrochemical treatment, reverse osmosis, membrane technologies and evaporation recovery. These processes may be ineffective or extremely expensive especially when metals in solution are in the range of 1–100 mg/L [4]. Another major disadvantage with conventional treatment technologies is the production of toxic chemical sludge and its disposal/treatment becomes a costly affair and is not eco-friendly. Therefore, removal of toxic heavy metals to an environmentally safe level in a cost effective and environment friendly manner, assumes great importance [5]. Biosorption refers to different modes of non-active metal uptake by biomass, where metal sequestration by cells can take place through biosorption, ion exchange, coordination, complexation, etc. [6]. The major advantages of biosorption over conventional treatment methods include, low cost; high efficiency; minimization of chemical or biological sludge; no additional nutrient requirement; possibility of regeneration of biosorbent and metal recovery [7]. Both living and dead biomasses exhibit biosorption capacity. In addition, living cells are subject to the toxic effects of heavy metals reaching a certain level, resulting in cell death. To

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[*] Corresponding author. Fax: +92 41 9200764.
E-mail address: hnbhatti2005@yahoo.com (H.N. Bhatti).

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overcome the disadvantages, non-viable or dead biomass is preferred in removal of metal ions [8]. Modification of a biomass using physical pretreatment methods such as heating, autoclaving, freezing, drying, boiling and chemical pretreatments such as using acids, alkalis and organic chemicals showed enhancement or reduction in metal biosorption [9].

Rosa gruss an teplitz (red rose) belongs to the class Bourbon. It is among one of the most extensively used flowers for steam distillation process. Biomass left after the extraction of rose oil and rose water using steam distillation is a waste material. In continuation of our work on removal of heavy metals from aqueous solutions (1, 7, 8, and 9), the present study is aimed at selection of a low cost biosorbents which can adsorb Zn(II) and Cu(II) from synthetic solutions. Detailed batch studies with the selected biosorbent, red rose distillation sludge, has been carried out in the present investigation. The effect of different experimental parameters such as pH, biosorbent dose, biosorbent size, initial metal concentration, shaking speed and contact time and various pretreatments on Zn(II) and Cu(II) uptake capacity of *R. gruss an teplitz* waste biomass was also investigated.

2. Materials and methods

2.1. Preparation of biosorbent

R. gruss an teplitz (red rose) biomass (distillation sludge) was obtained from Rose Laboratory, Institute of Horticultural Sciences, University of Agriculture, Faisalabad, Pakistan, and was extensively washed with deionized distilled water (DDW) to remove particulate material from their surface, and sun dried. Dried biomass was ground using food processor (Moulinex, France) and sieved (0.250–1.00 mm) by passing through sieving machine (Octagen Siever OCT-Digital 4527-01). Biosorbent was physically modified using heating (5 g of biosorbent was heated in oven at 60 °C for 30 min) and boiling (5 g of biosorbent/100 mL of H_2O, boiled for 10 min). For chemical pretreatments, 5 g of biomass was soaked in 100 mL of 0.1N HCl, 0.1N HNO_3, 0.1N H_2SO_4, 0.1N NaOH, 0.1N $Al(OH)_3$, sodium alginate (50 mL), PEI + glutaraldehyde (50 mL each), 1% *Moringa olifera*, 2% calcium alginate (50 mL), 1% glutaraldehyde (50 mL), 1% potash alum, 0.1N EDTA, 0.1N ethanol, 0.1N benzene, 0.1N methanol, 0.1N formaldehyde, 1% PEI (50 mL), acetone, 1% κ-carragnen, 1% Triton X-100 for 2 h. CO_2 and H_2S gas was passed through 5 g of biomass soaked in 100 mL of DDW at the rate of 10 mL/min for 10 min. All pretreated samples were allowed to stand for an hour at 30 °C. Then they were extensively washed with distilled water (DDW) and filtered thoroughly. Finally the biomass was oven dried at 30 °C for 48 h and ground with mortar and pestle and kept in airtight jars. The biomass was digested by wet digestion method ($HNO_3 + H_2O_2$) to determine its mineral composition.

2.2. Reagents

All the reagents used in this study were of analytical grade, including $ZnSO_4 \cdot 7H_2O$ and $CuSO_4 \cdot 5H_2O$ which were purchased from Fluka chemicals except *M. olifera* seed powder which was purchased from Super Market, Faisalabad, Pakistan.

2.3. Zn(II) and Cu(II) solutions

Stock Zn(II) solution (1000 mg/L) was prepared by dissolving 4.41 g of $ZnSO_4 \cdot 7H_2O$ and stock Cu(II) solution (1000 mg/L) was prepared by dissolving 3.95 g of $CuSO_4 \cdot 5H_2O$ in 1000 mL of DDW. The pH of stock solution of $ZnSO_4 \cdot 7H_2O$ was 3.71 and that of $CuSO_4 \cdot 5H_2O$ was 3.20. The solutions of different concentrations were prepared by adequate dilutions of stock solution with DDW.

2.4. Batch biosorption studies

All glassware used for experimental purpose was washed with 60% (v/v) nitric acid and subsequently rinsed with DDW to remove any possible interference by other metals. Batch tests were carried out in 250 mL shake flasks to check the influence of starting metal concentration (25–800 mg/L), biomass concentrations (0.05, 0.1, 0.2, 0.3 and 0.4 g per 100 mL), biosorbent particle size (0.250, 0.310, 0.500, 0.710 and 1.00 mm), contact time (15, 30, 60, 120, 240, 480, 720, and 1440 min), temperature (30, 40, 50, 60 and 70 °C), shaking speed (0, 50, 100, and 150 rpm) in order to check the possible maximum removal of metal ions. Control assay was accompanied with each experiment. At the end of each experiment, flasks were removed from the shaker and solutions were separated from the biomass by filtration through filter paper (Whatman no. 40, ashless).

For adjusting pH of the medium 0.1N solutions of NaOH and HCl were used.

2.5. Determination of Zn(II) and Cu(II) contents in solutions

Perkin-Elmer AAnalyst 300 Atomic Absorption Spectrometer equipped with an air–acetylene burner and controlled by Intel personal computer was used to determine concentrations of Cu(II) and Zn(II) in aqueous solutions before and after sorption equilibrium established. The analytical wavelengths used for Zn(II) and Cu(II) were: 213.9 and 327.4 nm, respectively.

2.6. Metal uptake and % sorption

Cu(II) and Zn(II) uptake was calculated by simple concentration difference method. Uptake of Cu(II) and Zn(II) was calculated from the mass balance equation [1]:

$$q_e = \frac{V(C_i - C_e)}{m}$$

where V is the volume of the solution (L), C_i is the initial concentration (mg/L), C_e is the final concentration in solution (mg/L) and m is mass of the sorbent (g).

% sorption is given as

$$\%\,\text{sorption} = \frac{C_i - C_e}{C_i} \times 100$$

2.7. Statistical analysis

Mean and standard deviation values were calculated from triplicate sets of experiments. All statistical analysis was performed using Microsoft Excel 2007, Version office Xp.

3. Results and discussion

3.1. Effect of pH

Experiments concerning the effect of pH on sorption were carried out within pH range that was not influenced by metal precipitation (as metal hydroxide). The suitable pH ranges for two metal ions were slightly different, i.e. experiments for Cu(II) sorption were performed at the pH range of 1–5 and for Zn(II) at pH of 1–6. The biosorption of Cu(II) and Zn(II) on the *R. gruss an teplitz* (red rose) distillation sludge biomass was observed to be the function of