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Concurrent sorption of Zn(II), Cu(II) and Co(II) by *Oscillatoria angustissima* as a function of pH in binary and ternary metal solutions

Harapriya Mohapatra, Rani Gupta *

Department of Microbiology, University of Delhi South Campus, Benito Juarez Road, New Delhi 110 021, India

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Abstract

This paper reports biosorption of Zn(II), Cu(II) and Co(II) onto *O. angustissima* biomass from single, binary and ternary metal solutions, as a function of pH and metal concentrations via Central Composite Design generated by statistical software package Design Expert® 6.0. The experimental design revealed that metal interactions could be best studied at lower pH range i.e. 4.0–5.0, which facilitates adequate availability of all the metal ions. The sorption capacities for single metal decreased in the order Zn(II) > Co(II) > Cu(II). In absence of any interfering metals, at pH 4.0 and an initial metal concentration of 0.5 mM in the solution, the adsorption capacities were 0.33 mmol/g Zn(II), 0.26 mmol/g Co(II) and 0.12 mmol/g Cu(II). In a binary system, copper inhibited both Zn(II) and Co(II) sorption but the extent of inhibition of former was greater than the latter; sorption values being 0.14 mmol/g Zn(II) and 0.27 mmol/g Co(II) at initial Zn(II) and Co(II) concentration of 1.5 mM each, pH 4.0 and 1 mM Cu(II) as the interfering metal. Zn(II) and Co(II) were equally antagonistic to each others sorption; Zn(II) and Co(II) sorption being 0.23 and 0.24 mmol/g, respectively, at initial metal concentration of 1.5 mM each, pH 4.0 and 1 mM interfering metal concentration. In contrast, Cu(II) sorption remained almost unaffected at lower concentrations of the competing metals. Thus, in binary system inhibition dominance observed was Cu(II) > Zn(II), Cu(II) > Co(II) and Zn(II) ~ Co(II), due to this the biosorbent exhibited net preference/affinity for Cu(II) sorption over Zn(II) or Co(II). Hence, the affinity series showed a trend of Cu(II) > Co(II) > Zn(II).

In a ternary system, increasing Co(II) concentration exhibited protection against the inhibitory effect of Cu(II) on Zn(II) sorption. On the other hand, the inhibitory effect of Zn(II) and Cu(II) on Co(II) sorption was additive. The model equation for metal interactions was found to be valid within the design space.

Keywords: Single sorption; Binary sorption; Ternary sorption; Zinc; Copper; Cobalt; Multimetal; pH; Biosorption

1. Introduction

Past two decades has witnessed a drastic increase in the quality and quantity of metal pollutants discharged into aqueous environmental sink. Major nuisance of metal pollution results from the activities of metal based small-scale industries engaged in electroplating, galvanization, alloy making, manufacture of non-ferrous casting, batteries etc. Such industries due to low returns constrain themselves from investing in the area of effluent treatment (Volesky, 1990). Zinc and copper are the most extensively used metals by these small-scale industries, while cobalt is generally associated with them as a contaminating material. Though Zn, Cu and Co are potentially less toxic, special care needs to be taken in order to prevent the cumulative accumulation of these metals in the environmental sink. The process of microbial

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* Corresponding author. Tel.: +91 011 26111933; fax: +91 011 26885270.
E-mail addresses: ranigupta15@rediffmail.com, ranigupta15@yahoo.com (R. Gupta).

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metal removal by biosorption is a well documented phenomenon (Gadd, 1988; Brierley, 1990; Greene and Darnall, 1990; McLean and Beveridge, 1990; Volesky, 1990; McHale and McHale, 1994; Volesky and Holan, 1995; Kapoor and Viraraghavan, 1995; Wase and Foster, 1997; Gupta et al., 2001). Biosorption also provides a cheaper alternative for metal removal from dilute solutions—both in batch and continuous cultures, for these economically constrained small-scale industries. Immobilized biosorbent has an added advantage of being an easily recyclable material; thus is a one-time investment. In general selection of matrices should be done such that they do not hamper or slow down the sorption capacity of the biomass by blocking or consuming the binding sites (Bedell and Darnall, 1990; Gupta and Mohapatra, 2003).

A practical consideration to the problem reveals that most of the effluent solutions represent a case of multimetal situation rather than monometal situation. In such a scenario it becomes essential to study the effect of the presence of co-cations on the biosorption capacity of the biosorbent (Schiewer and Volesky, 2000; Veglio et al., 2003). Secondly, there also occurs a wide variation in the pH of the effluents. The pH of the system plays an important role in the affecting the ionic state and hence the availability of the binding sites (Schiewer and Wong, 2000). The application of mathematical models to biosorption processes apart from giving a quantitative description of the process also aid in optimizing the operating conditions. Secondly, mathematical modeling at bench scale levels help in minimizing the number of experimental runs and help to pin-point the results of spot check experiments (Schiewer and Volesky, 2000). Thirdly, modeling at industrial scale becomes indispensable as it goes a long way in reactor designing and helps discover bottlenecks thereby optimizing the operational conditions and reducing the costs involved in hit and trial runs.

Much of the work done in multimetal studies have focused on metal sorption in binary system using multicomponent Langmuir or Freudlich isotherm models (Chong and Volesky, 1995; Schiewer and Volesky, 1995; Figueira et al., 1997; Sag et al., 1998, 2000; Sanchez et al., 1999; Benguella and Benaissa, 2002; Ma and Tobin, 2003; Li et al., 2004; Lee et al., 2004). Comparatively less literature is available on concurrent metal sorption from ternary systems (Chong and Volesky, 1996; Figueira et al., 2000; Sag et al., 2001). These methods are lengthy, complicated and are two parameter models which are 'not structured' i.e. they do not reflect the mechanism well (Volesky, 2003). A relatively simpler approach has been reported by Mehta and Gaur (2001) by the use of two-dimensional contour plots using graphical software Sigma Plot 2.0 to evaluate the behaviour of the biosorbent in a binary metal solution. This has a limitation of using a maximum of two-factors at a time.

In this paper, we report biosorption of Zn(II), Cu(II) and Co(II) onto *O. angustissima* immobilized biomass from single, binary and ternary metal solutions, as a function of pH and metal concentrations via response surface methodology using Central Composite Design (CCD) generated by the statistical software package Design Expert® 6.0. This design overcomes the limitations of earlier approaches and can accommodate as many as eight numerical variables at a time. For the result analysis of any multivariate experimental run conducted by Design Expert, the algorithmic software has been designed such that it takes care of the effects of each and every factor in the process. Though the package is a common tool amongst enzymologist for media optimization and kinetic constant studies, to the best of our knowledge this is the first report of the use of this statistical software for predicting the metal sorption capacities.

2. Methods

2.1. Procurement, growth and maintenance of culture

Cyanobacterial culture of *Oscillatoria angustissima* (ARM 783) was procured from the National Facility for Blue–Green Algae, Indian Agriculture Research Institute, New Delhi. The culture was sub-cultured and maintained on BG 11 minimal medium (Stanier et al., 1971) supplemented with $NaNO_3$ at a concentration of 1.5% w/v as the nitrogen source.

2.2. Immobilization of the biomass

The biomass was immobilized by modified method of Nemec et al. (1977). Two gram of fat free casein (SRL, Mumbai, India) was allowed to swell by addition of 4 ml of water. Fresh biomass was added to the pre-swollen casein at matrix: biomass ratio of 1:1 and mixed in a mortar-pestle. Following this 5 ml of 12% formaldehyde was added and mixed. This mixture was cured at 80 °C for 8–10 h and crushed to powder after drying and stored in an airtight container for further use. Biosorption by immobilized biomass and the immobilization matrix was compared by paired *t*-test using statistical software STATISTICA® 6.0 (Statsoft Inc., USA). Metal removal by immobilized biomass was significantly higher than the immobilization matrix at $p < 0.05$ (data not shown).

2.3. Stock solutions of heavy metal

Metal stock solutions of a concentration of 0.2 M (10,000 mg/L) were prepared by dissolving calculated amount of their salts in double distilled water. Zinc and copper were used as their sulfate salts while cobalt