Cadmium (II) ion and nickel (II) ion biosorption on yeast: Application of equilibrium model

Padma Vasudevan1,*, V Padmavathy2 and S C Dhingra3
1Centre for Rural Development and Technology,
2Department of Chemical Engineering, Indian Institute of Technology Delhi, New Delhi, 110 016
31101 Wilson Road, Conroe, 77301, Texas

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Experimental data on cadmium (II) and nickel (II) ion sorption on deactivated protonated yeast over a wide range of sorbent and initial metal concentrations, were analyzed by an equilibrium model based on a thermodynamics approach. Model describes relationships between the equilibrium concentration of metal, metal sorption per unit biomass dosage and concentration of sorbent and initial metal concentrations at constant pH and temperature. It is not found possible to reasonably fit the sorption data for cadmium (II) and nickel (II) ion on deactivated protonated yeast, to a unique isotherm curve when both initial metal ion concentration and biomass concentration are varied at a particular pH. Model fits the data well for the sorption of nickel (II) ion onto deactivated protonated yeast at pH 6.75. However, model could be applied only for a given substrate concentration for sorption of cadmium (II) ion onto sodium form of deactivated protonated yeast at pH 6.5.

Keywords: Biosorption, Cadmium, Equilibrium model, Nickel, Wastewater treatment, Yeast

Introduction

Heavy metal sorption on different types of microbial biomass, bacteria, fungi and algae in particular, both in live and nonviable forms1 are being studied extensively. However, appropriate predictive mathematical models are not available for describing the equilibrium behavior of metal-sorbent systems. Langmuir and Freundlich sorption isotherms2-7, are now seen to be descriptive rather than predictive. In most cases, researchers have kept the amount of sorbent constant for varying initial metal concentrations and less commonly, have varied sorbent amount for a fixed metal concentration. When both the sorbent and metal concentrations are changed, these models fail to give one universal curve8-10. Gin et al11 analyzed these issues and proposed a new model based on thermodynamics of sorption as:

\[ \frac{C_e}{C_o} = \alpha \exp\left(\beta \frac{M}{C_o}\right) \]  \hspace{1cm} (1)

where \( C_o \) = initial concentration of heavy metal ion in solution, \( C_e \) = equilibrium concentration of metal ion in solution after sorption, \( M \) = concentration of biomass, \( \beta = \) negative constant and reflects the metal sorption ability of the biomass, and \( \alpha = \exp(\Delta G^o/RT) \) is also a constant where \( \Delta G^o \) is the standard free energy change.

Other forms of equations, which follow from Eq. 1, are:

\[ \frac{x}{m} = 1 - \frac{\alpha \exp(\beta M/C_o)}{M/C_o} \]  \hspace{1cm} (2)

\[ \frac{x}{m} = \beta \frac{1 - C_e/C_o}{\ln(Ce/\alpha C_o)} \]  \hspace{1cm} (3)

where \( m \) is the mass of biomass taken in volume (V) of solution and \( x \) is the total weight of metal ion sorbed on \( m \) (\( m = M^*V \)).

Present model differs from Freundlich and Langmuir sorption models in that the latter only incorporate \( C_e \) and not \( C_o \). The model has been applied to several metal sorption systems on algal biomass. In the present paper, applicability of the thermodynamic model to experimental data on cadmium (II) ion and nickel (II) ion sorption on yeast over a wide range of sorbent and initial metal concentration is analyzed.

*Author for correspondence
E-mail: padmav10@hotmail.com, vp_12@yahoo.com
Materials and Methods
Preparation of Biosorbent
Yeast biomass procured from SAF yeast Co. Ltd., Chembur, Mumbai, India, was deactivated by heating in an oven at 80°C for 24 h. For pretreatment of biomass, a sample of finely ground deactivated native biomass (10 g) was taken and treated with 0.1 M HCl solution (1000 ml) for 24 h. Biomass was washed several times with distilled water to remove excess acid and then oven dried at 60°C for 24 h to yield protonated biomass. This was used as a simple uniform sorption system, for nickel (II) ion adsorption involving only H⁺ ion and nickel (II) ion, as washing with HCl elutes all other sorbed metal ions in the native biomass. For cadmium (II) ion adsorption, protonated biomass was further converted into sodium form, by treating with an excess of sodium acetate and acetic acid. Biomass was then washed with distilled water several times and dried at 60°C for 24 h. Stock metal ion solutions were prepared by taking cadmium sulfate and nickel sulfate (Qualigens fine Chem., Mumbai) of analytical grade and then dissolved in appropriate amounts of distilled water.

Biosorption Studies
Biosorption of Ni from varying concentrations of nickel solution on 100 mg/l of adsorbent, studied at varying pH (2-6 & 6.75), was maximum at pH 6.5. Similarly, studies conducted for different concentrations of cadmium at varying pH (2-6, 6.5 & 7), maximum sorption was at pH 7.5. Subsequently, equilibrium sorption experiments were carried out, varying both the initial metal and biomass concentrations, maintaining optimal pH for each system. For cadmium (II) ion sorption experiments, initial metal ion concentration was varied (10-500 mg/l) and the biomass concentrations were varied (1000-80000 mg/l) keeping initial pH at 6.5. The pH was adjusted to the required value using 0.2 M sodium acetate and /or acetic acid before the addition of the sorbent, and was kept constant during the experiment by the addition of 0.1 N NaOH or 0.2 N acetic acid as required. Nickel (II) sorption experiments were performed at an optimum pH (6.75) by varying the metal ion concentrations (10-1000 mg/l) and also the biomass concentrations (500-8000 mg/l). The pH of the solution was constantly measured and adjusted using 0.01 N NaOH/HCl.

Mixtures were continuously stirred on a rotary shaker at 120. After 24 h, biosorbent was then separated from the respective solutions by centrifugation and filtration. Concentration of nickel (II) ion in the sample solution was determined spectrophotometrically in the form of its complex with dimethylglyoxime. Residual cadmium (II) ion concentration in the solution was measured using an atomic absorption spectrophotometer either directly or by diluting the samples with double distilled water so as to allow the concentration of metal to be within the measuring range of the instrument.

Further, the collected sorbent portions were also dried. Metal ion was leached out with 3 M HNO₃ (10 ml) for 20 min and analyzed. Thus, the amount of metal biosorbed was determined both from its loss from the solution and elution of the amount bound by the sorbent. All experiments were conducted in triplicate. Blanks without biosorbent were run simultaneously as control. Maximum variation in metal sorption data between triplicate experiments was 5 %. Mean value for the replicates was used for comparisons.

Results and Discussion
Application of Model: Nickel (II) Ion Sorption
In the sorption isotherm data (q = x/m vs Cₑ) for nickel (II) ion on protonated form of deactivated yeast (Fig. 1), obtained at different initial metal ion concentrations (10-1000 mg/l) and different biomass concentrations (500-8000 mg/l) under a constant pH (6.75), q represents the amount of metal ion sorbed per
unit weight of biomass and $C_e$ the metal ion concentration remaining in solution at equilibrium. Varying $C_o$ and $M$, all the data do not fit into one isotherm. However, plots for a given $M$ are on one curve. A linearized plot of Langmuir with a correlation coefficient of 0.993 has been obtained when initial nickel (II) ion concentrations ($C_o$) is varied, keeping biomass concentration constant (1000mg/l).

Experimental data was plotted as $\ln \left( \frac{C_e}{C_o} \right)$ vs $M/C$, (Fig. 2), to test the linear form of Eq. (1). Data points fit into a single linear plot showing the applicability of the model. Correlation coefficient for the observed straight line is 0.9908. Values of $\alpha$ (0.9813) and $\beta$ (–0.0059) were obtained from intercept and slope of the linear form of Eq. (1). While $\beta$ reflects metal sorption ability of biomass, $\alpha$ should take a value of 1 under ideal conditions. Similar values of $\alpha$ and $\beta$ have been reported\textsuperscript{11} taking other metal-sorbent systems.

### Application of Model: Cadmium (II) Ion Sorption

Sorption isotherm data ($q = x/m$ and $C_e$) for cadmium (II) ion (Fig. 3), obtained at different initial metal ion concentrations (10-500mg/l) and different biomass concentrations (1000-80000 mg/l) under a constant pH (6.5), shows (Table 1) that the data points do not fit into one curve, rather a separate curve is obtained for each biomass concentration, $M$. It has been reported\textsuperscript{10} that a unique curve as per Langmuir model was not obtained for cadmium (II) ion sorption on varying sorbent concentration. Similar behaviour is reported\textsuperscript{11,12} for the sorption of cadmium (II) ion by

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![Fig. 2](image1.png)  
Fig. 2—Plot of in (Ce/Co) vs M/C; Ion sorption by deactivated protonated yeast with different initial metal and biomass conc. at initial pH 6.75

![Fig. 3](image2.png)  
Fig. 3—Plot of $x/m$ vs C; Ion sorption by deactivated protonated yeast with different initial metal and biomass conc. at initial pH 6.75
algal biomass when both different initial metal concentration and biomass dosage were used for the same set of experiments.

Experimental data was plotted as ln $\left(\frac{C}{C_0}\right)$ vs $\frac{M}{C_0}$. Unlike in the case of nickel (II) ion, no single straight line was obtained covering all the points. However, points corresponding to a given mass of sorbent, $M$, with varying initial concentrations (Fig. 4), do fall on a straight line. Separate straight lines were thus observed for each mass of sorbent, $M$. Unlike in the case of nickel (II) ion, $\alpha$ values are seen much below 1 (Table 2). Also while there is no specific trend with varying $M$, $\alpha$ values were 0.1535-0.2080.

Gin et al.\textsuperscript{11} observed that Eq. 1 is able to fit their experimental data reasonably well for the sorption of cadmium (II) ion and copper (II) ion on the algal biomass of both Oocystis sp. and Chlorococcum sp. (either in living or dead form) at different pH. The trend of present experimental data for sorption of cadmium (II) ion on to the sodium form of deactivated yeast may possibly be explained in terms of existence of several absorption sites with different sorption energies. The sorption on these sites may be occurring by more than one mechanism such as ion exchange and coordination. Earlier studies\textsuperscript{10} on kinetics have also indicated a similar possibility of presence of more than one site with different energy levels.

Conclusions

It was not possible to reasonably fit the sorption data for cadmium (II) ion and nickel (II) ion on deactivated protonated yeast, to a unique isotherm curve when both initial metal ion concentration and biomass concentration were varied at a particular pH. However, a Langmuir plot is obtained for a given biomass concentration ($M$) held constant. Thermodynamic model gave a good fit to the data for sorption of nickel (II) ion onto deactivated protonated yeast at a pH of 6.75. Values of $\alpha$ and $\beta$ were found to be 0.9813 and $-0.0059$ respectively. For sorption of cadmium (II) ion onto sodium form of deactivated yeast at a pH of 6.5, model could be applied only for a given substrate concentration. Several sorption modes may be operative involving ion exchange and coordination.

References