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Biosorption of Co(II) by *Schizosaccharomyces pombe*: Kinetic and Thermodynamic Studies for Process Design

Nihat Alpagu Sayar, Selcen Durmaz-Sam, Gizay Odabasi and Ahmet Alp Sayar*

Department of Bioengineering, Marmara University, Kadikoy 34722, Istanbul, Turkey

Abstract

The characterisation of biosorption by *Schizosaccharomyces pombe* of Co(II) was done under varying experimental conditions including pH, temperature, initial metal concentration and biosorbent dose. Optimum pH was found to be 5.0 with optimal biosorbent dose for highest adsorption capacity at 1.0 g L^{-1}. Higher initial metal concentrations helped enhance q_e slightly with the highest value, 2.7 mg g^{-1}, being achieved at 25°C and 50 mg L^{-1} initial Co(II). Temkin isotherm model showed the best statistical fit for equilibrium data while Freundlich isotherm model exhibited thermodynamic consistency. Pseudo-first order kinetics was found to represent Co(II) biosorption. Increasing ΔG^0 values calculated with respect to higher operational temperatures were in agreement with kinetic profiling simulations whereby higher temperatures were found to be less favourable. Overall efficiency of *S. pombe* as a biosorbent for Co(II) was found to be significantly less than Ni(II), for this reason it can be regarded as a potential bioseparation agent for aqueous mixtures containing both Co(II) and Ni(II).

Keywords: Biosorption; *Schizosaccharomyces pombe*; Adsorption isotherms; Process thermodynamics, Biokinetics; Separation

Nomenclature

A_0	Frequency factor
A_T	Temkin isotherm equilibrium constant, L g^{-1}
b_K	Khan isotherm constant
b_T	Temkin isotherm constant
C_e	Residual aqueous metal concentration at equilibrium, mg L^{-1}
C_i	Initial aqueous metal concentration, mg L^{-1}
E_a	Activation energy, kJ mol^{-1}
k	Kinetic rate constant
K_{eq}	Selected isotherm equilibrium constant
K_F	Freundlich isotherm equilibrium constant, L mg^{-1}
K_L	Langmuir isotherm equilibrium constant, L mg^{-1}
k_{p1}	Pseudo-first order rate constant, min^{-1}
k_{p2}	Pseudo-second order rate constant, g mg-1 min^{-1}
K_{RP}	Redlich-Peterson isotherm equilibrium constant, L g^{-1}
K_S	Sips isotherm equilibrium constant, (mg g^{-1}) (mg $L^{-1})^{-\beta}$
m	Amount of biosorbent, g
n_F	Freundlich isotherm exponent
n_K	Khan isotherm exponent
q_0	Maximum metal uptake, mg g^{-1}
q_e	Equilibrium metal uptake, mg g^{-1}
q_i	Initial metal uptake rate, mg g^{-1}
q_t	Metal uptake at t, mg g^{-1}
R	Universal gas constant, 8.314 J mol^{-1} K^{-1}
R^2	Correlation coefficient
RMSE	Root mean square error
T	Time, s or hr
T	Temperature, K
V	Volume of aqueous phase, L
α_{RP}	Redlich-Peterson isotherm constant
α_S	Sips isotherm constant, (L $mg^{-1})^{\beta}$
β_{RP}	Redlich-Peterson isotherm exponent
β_S	Sips isotherm exponent
ΔG^0	Gibbs free energy change, J mol^{-1}
ΔH^0	Enthalpy change, J mol^{-1}
ΔS^0	Entropy change, J mol^{-1} K^{-1}

Introduction

Biosorption of heavy metal ions from aqueous solutions is an area where there are growing interest and success [1]. Previous studies have shown that wild-type *Schizosaccharomyces pombe* is a promising agent for the biosorption of nickel(II) from aqueous solutions [2]. Considering the fact that in most naturally and technologically relevant conditions cobalt(II) is found along with nickel(II), it is a logical undertaking to investigate the biosorption properties of wild-type *S. pombe* for cobalt(II) for both biohydrometallurgical separation and environmental control purposes.

***Corresponding author:** Ahmet Alp Sayar, Department of Bioengineering, Marmara University, Kadikoy 34722, Istanbul, Turkey, Tel: 90-216-348 0295, ext. 718; Fax: 90-216-345 01 26;Email: asayar@marmara.edu.tr

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A variety of biological materials have been examined as biosorption agents for Co(II). Among these are marine algae *Ascophyllum nodosum* [3], crab shell particles [4], fungi of genera *Aspergillus, Rhizopus* [5] and *Saccharomyces* [1]. This study focuses on the biosorptive properties of *S. pombe* on Co(II). Advantages of using this organism are its rapid growth rate, high biomass yield and non-pathogenic character. These advantages also ensure cheaper and easier production at large scales.

It also has to be noted that there has been mounting interest in using membrane processes for the separation of cobalt and nickel in aqueous solutions. The reported separation factors achieved using some of these processes are very high, with examples like 80 [6] or 250 [7]. Although such values are seemingly remarkable, one has to keep in mind that membrane technology displays some serious disadvantages in terms of industrial application such as scale-up and staging difficulties and membrane fouling. Therefore, adsorption and solvent extraction methods for the separation of heavy metals still hold primary importance in scientific research and industrial applications.

Characterisation of biosorption properties is an essential prerequisite for further design studies towards industrial application of such processes. Characterisation of the biosorbent properties of *S. pombe* for Co(II) comprises the main aim of the current paper. Fundamental aspects for such a characterisation include equilibrium, kinetic and thermodynamic analyses of the biosorption process. Effects of pH, initial aqueous metal concentration and biosorbent dose also constitute the key aspects of such a study. On top of these conventional and generally performed investigations, the scope of this study also covers the kinetic profiling of and preliminary design calculations for a single stage batch biosorber.

The biosorption of Co(II) by *S. pombe* is presumed to happen via a passive ion exchange process between the aqueous metal and the cellular surface of the biosorbent. Process parameters such as the pH and temperature and initial biomass and metal concentrations in the aqueous media affect the binding between the organism and the metal. Accordingly, these parameters are to be examined in order to assess the feasibility of an industrial application [8]. Industrial feasibility assessment and comparison with alternative systems also require an understanding of the performance of the system for which kinetic information and preliminary design calculations are informative [9].

The biosorption characterisation procedure follows the single sorbate-simple closed batch system methodology. The details of this approach are available in a previous study [2]. The equilibrium values of Co(II) uptake by the biomass, q_e, mg (g dry weight)$^{-1}$ can be calculated using:

$$q_{\mathrm{e}} = \frac{(C_{\mathrm{i}} - C_{\mathrm{e}})V}{m} \tag{1}$$

where C_i, C_e, V and m denote, initial Co(II) concentration of the aqueous phase (mg L^{-1}), equilibrium Co(II) concentration of the aqueous phase (mg L^{-1}), volume (L) of the solution contacted with sorbent and the amount of the sorbent expressed as dry mass (g), respectively.

Adsorption isotherms were used for the assessment and evaluation of biosorption of Co(II) onto *S. pombe*. These isotherms can be further employed during the preliminary equipment design for a relevant industrial process. Six different adsorption isotherm models were considered for this study. Langmuir, Freundlich, Langmuir-Freundlich (Sips) and Redlich-Peterson isotherms were chosen since they are the most studied and best understood models. Khan and Temkin isotherms [10] were also included. Khan isotherm shows characteristic similarities to the above-mentioned ones, thus offers a possibility of a good fit. Although it is argued elsewhere that Temkin isotherm might not be appropriate for complex adsorption systems including liquid-phase adsorption [11]; Temkin isotherm features a linear dependency to biosorption heat which is in agreement with the observations made of the present system. Mathematical descriptions of these isotherm models can be found in Table 1. Once an isotherm is found to be satisfactorily descriptive of the studies it will be used in an elementary design of a single-stage batch biosorber.

Another important aspect of the characterisation of biosorption is an adequate description of the kinetics of the interaction between the biosorbent and the adsorbate. Pseudo-first or pseudo-second order kinetics is usually found to be adequately descriptive of the biosorption phenomenon [1]. Relevant rate equations are given in Table 2. The appropriate rate equations that describe the currently studied system will be used in a preliminary modelling scheme to simulate the kinetic biosorption profiles.

The third essential part of biosorbent characterisation is the thermodynamic analysis of the process, in terms of feasibility and energy consumption studies as a precedent for industrial design approaches. Thermodynamic functions such as activation energy, Gibbs free energy change, enthalpy and entropy changes are crucial for process design calculations. The activation energy, E_a in kJ mol^{-1}, can be calculated using:

$$\ln k = \frac{-E_{\mathrm{a}}}{RT} + \ln A_0 \tag{2}$$

The calculated value for E_a is an index to be used to distinguish if the biosorption in question is either of a physical or a chemical nature. ΔG^0 can be calculated by:

$$\Delta G^0 = -RT \ln K_{\mathrm{eq}} \tag{3}$$

Biosorption isotherm	Formulae
Langmuir	$q_{\mathrm{e}} = \frac{q_0 K_{\mathrm{L}} C_{\mathrm{e}}}{1 + K_{\mathrm{L}} C_{\mathrm{e}}}$
Freundlich	$q_{\mathrm{e}} = K_{\mathrm{F}} C_{\mathrm{e}}^{1/n_{\mathrm{F}}}$
Langmuir-Freundlich (Sips)	$q_{\mathrm{e}} = \frac{K_{\mathrm{S}} C_{\mathrm{e}}^{\beta_{\mathrm{S}}}}{1 + \alpha_{\mathrm{S}} C_{\mathrm{e}}^{\beta_{\mathrm{S}}}}$
Redlich-Peterson	$q_{\mathrm{e}} = \frac{K_{\mathrm{RP}} C_{\mathrm{e}}}{1 + \alpha_{\mathrm{RP}} C_{\mathrm{e}}^{\beta_{\mathrm{RP}}}} c$
Khan	$q_{\mathrm{e}} = \frac{q_0 b_{\mathrm{K}} C_{\mathrm{e}}}{(1 + b_{\mathrm{K}} C_{\mathrm{e}})^{n_{\mathrm{K}}}}$
Temkin	$q_{\mathrm{e}} = \frac{RT}{b_{\mathrm{T}}} \ln(A_{\mathrm{T}} C_{\mathrm{e}})$

Table 1: Isotherm models applied to the biosorption data.

Kinetic model	Differential form	Integrated form
Pseudo-first order	$\frac{dq}{dt} = k_{p1}(q_e - q_t)$	$\log(q_e - q_t) = \log q_e - \frac{-k_{p1}}{2.303} t$
Pseudo-second order	$\frac{dq}{dt} = k_{p2}(q_e - q_t)^2$	$q_t = \frac{t}{\frac{1}{k_{p2} q_e^2} + \frac{t}{q_e}}$

Table 2: Kinetic models applied to the biosorption data.

where R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature in Kelvin; K_{eq} (selected equilibrium constant) used in L mol^{-1}. By employing the selected equilibrium constant, the following linear thermodynamic relation can be obtained:

$$\ln K_{eq} = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \qquad (4)$$

Materials and Methods

Preparation of the biosorbent

The wild-type strain of *S. pombe (972 h)* obtained from University of Istanbul, Deparment of Molecular Biology and Genetics, Turkey, was first cultivated, then harvested and finally prepared to be used as biosorbent in this study. For the cultivation of yeast cells, cultures on agar slants were used to inoculate 100 ml of sterile preculturing medium consisting of 30 g L^{-1} glucose and 5 g L^{-1} yeast extract. Preculturing medium was incubated at 30°C by shaking at a rate of 180 rpm until the early stationary growth phase which was determined by the intermittent spectrophotometric measurements of cell culture's optical density at 600 nm. Then, 200 ml of sterile media containing 30 g L^{-1} glucose and 5 g L^{-1} yeast extract in 500 ml Erlenmeyer flasks were inoculated with previously prepared preculture at an inoculum ratio of 1/100 (v/v). The flasks were agitated at 180 rpm at 30°C for 40 h when the optical density of cultures at 600 nm showed negligible changes. The yeast cells were separated from the media by centrifugation at 9,000 rpm for 3 min at 20°C. Liquid part was discarded and cell pellet was washed twice with ultra-pure grade water. In order to dry yeast cells the pellet was kept at 50°C for 72 h. Dried cell chunks were grinded with the help of a blender. Dry biomass was preserved in a desiccator until it was used in biosorption experiments.

Sterilization of all growth media and flasks was accomplished in an autoclave (OT 032 Nüve, Turkey) at 121°C and 1.0 atm for 15 min. Co(II) stock solution with a concentration of 1 g L^{-1} was prepared by dissolving a proper amount of $CoCl_2.6H_2O$ (Analytical Grade, Carlo Erba, France) in ultra-pure water.

Biosorption experiments

In order to determine the optimum pH for the current biosorption system, experiments were conducted at varying pH values. Five Erlenmeyer flasks (250 mL), each containing 100 mL of 10 mg L^{-1} Co(II) solution, were prepared and adjusted to pH 2.0, 3.0, 4.0, 5.0 and 6.0 (±0.1) respectively, by the addition of either 0.1 (or 1.0) N HNO_3 or 0.1 (or 1.0) N NaOH. Dry biomass of *S. pombe* cells was added to each flask to obtain a concentration of 1 g L^{-1}. The flasks were shaken for duration of 2 h at 150 rpm and 25°C. pH 5.0 ± 0.1 was found to be the optimal operating value used throughout the rest of the experiments.

Further experimentation was conducted using the abovementioned setup but with different initial metal concentration values (2.7 ± 0.1, 5.2 ± 0.2, 7.3 ± 0.2, 11.1 ± 1.1, and 53.8 ± 2.8 mg L^{-1}) and at various operational temperatures (25, 30, 35 and 50 ± 0.2°C). Samples were taken at predetermined time intervals and centrifuged for 5 min at 10,000 rpm and 20°C. Initial and residual Co(II) concentrations of the samples were measured using a Thermo Scientific Atomic Absorption Spectrophotometer (Model: iCE 3500) at 240.7 nm. All experiments were conducted in triplicate.

Results and Discussion

Effect of pH

The pH of the solution within which biosorption takes place influences both the metal and cell surface chemistry and thus is an important operational parameter for a biosorption process. Determination of the optimum pH value for the current Co(II) biosorption system was done by experimentation at 25°C whereby 10 mg L^{-1} Co(II) solutions with a biomass concentration of 1 g L^{-1} each and pH values ranging from 2.0 to 6.0 (by increments of 1.0) were used. pH values over 6.0 weren't considered due to the fact that no improvement on metal uptake was observed over pH 5.0. Figure 1 displays that optimum Co(II) uptake is attained at pH 5.0 where q_e equals 2.55 mg g^{-1}. Almost a linearly correlated increase in metal uptake accompanies the increasing pH of the medium from pH 2.0 to 5.0 where a peak is reached and a slow decline can be observed afterwards. An impressive ten-fold increase in metal uptake is achieved when working at pH 5.0 compared to pH 2.0. An increase in the pH might affect the ionic configuration of some of the functional groups esp. at the cellular surface and improve the interactions with the metal ions.

Effect of sorbent dose

Four experiments with different biosorbent concentrations were conducted to observe the effect of sorbent dose on metal uptake. 50 mg L^{-1} Co(II) solutions with 0.5, 1.0, 2.0 and 3.0 g L^{-1} *S. pombe* concentrations were used at 25°C and pH 5. Although the total amount of metal adsorbed increased with higher biosorbent concentrations (from 1.1 mg L^{-1} at the lowest biosorbent concentration to 6.2 mg L^{-1} at the highest); the adsorption capacity peaked at 1.0 g L^{-1} biosorbent concentration with a value of 2.7 mg g^{-1}. Figure 2 exhibits the trend with which metal uptake at equilibrium relates to biosorbent concentration. The reason why equilibrium metal uptake falls with very high biosorbent concentrations, contrary to expectation, may be due to increased electrostatic interactions between the cells which obstruct the contact between metal cations and cellular binding sites; since it cannot be due to the insufficiency of solute to cover all available binding sites considering the significant amounts of residual metal in solution at equilibrium, observed even at optimal uptake conditions. Over 50% of metal remains in solution under all conditions tested.

A techno-economic trade-off between the cost of biosorbent and the amount of metal adsorbed per unit of the biosorbent exists which a thorough cost-benefit analysis of these parameters may resolve but it

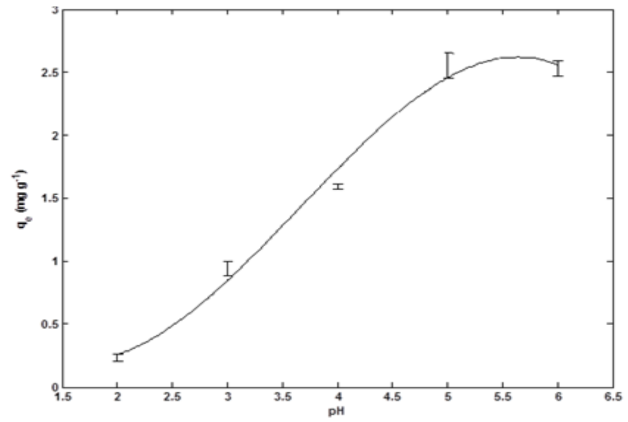

Figure 1: Effect of pH on the equilibrium uptake of Co(II) by *S. pombe* (Temperature: 25°C, initial Co(II) conc.: 10 mg L^{-1}, biosorbent dose: 1.0 g L^{-1}, agitation rate: 150 rpm. The *bars* represent standard deviation of the mean).

falls out of the scope of this study.

Equilibrium studies

Isotherm models: Elucidation of an appropriate biosorption equilibrium correlation is an essential component for reliable prediction of biosorption parameters and quantitative comparison and effective design of different biosorption systems [11]. Experimental equilibrium data of the Co(II) biosorption system was analysed using established isotherm models Langmuir, Freundlich, combined Langmuir-Freundlich (Sips), Redlich-Peterson, Khan and Temkin isotherms. Langmuir, Freundlich and Temkin are two-parameter models whereas the others have three parameters. The three-parameter Sips, Redlich-Peterson and Khan isotherms are modified versions of the Langmuir isotherm combining its features with that of Freundlich. Temkin isotherm is a two-parameter model including a term for temperature.

The correlation between the observed variables C_e and q_e has been analysed using Matlab R2012b's NonLinearModel fit function to determine the optimised values of the model parameters. The use of adjusted-R2 (square of the correlation factor) as statistical performance index is necessitated by the multivariate and nonlinear characteristics of the isotherm model equations. Additionally, root mean square error (RMSE) values for each fitted model are produced as a way to aid the statistical assessment. The results are tabulated in Table 3.

Across all experimentally observed conditions Temkin isotherm model exhibits the best fit statistically.

Effect of initial metal concentration on equilibrium metal uptake: Biosorption processes with varying initial metal concentrations between 2.5 and 50 mg L^{-1} were tested at four different operating temperatures. The experimental results are compared with Temkin isotherm models optimised with appropriate data in Figure 3. The plots show the effect of initial metal concentration, C_i, on the isothermal relationship between equilibrium values of C_e and q_e. An increase of initial metal concentration from 2.5 to 50 mg L^{-1} shows a positive effect, albeit very minor for initial metal concentrations above 10 mg L^{-1}, on the equilibrium values for all temperatures tested. It can be said that, above that level, either saturation of the binding sites on cell surfaces occurs or adsorptive (e.g. affinity between metal ions and cell surface) and desorptive (e.g. electrostatic repulsion between metal ions) forces balance. It has also to be noted that at these metal concentrations and pH value (5.0) precipitation of metal ions doesn't take place.

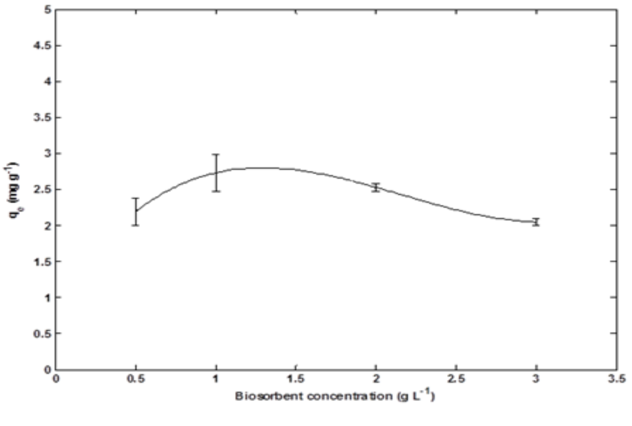

Figure 2: Effect of sorbent dose on equilibrium uptake of Co(II) by *S. pombe* (Temperature: 25°C, initial Co(II) conc.: 50 mg L-*1*, biosorbent dose: 1.0 g L^{-1}, agitation rate: 150 rpm. The *bars* represent standard deviation of the mean).

Combined effect of temperature and initial metal concentration: Figure 4 displays the combined effect of two independent process parameters, namely temperature and initial Co(II) concentration in solution on equilibrium metal uptake. Lower temperatures and higher initial concentrations seem to be favoured by the biosorption process. The kind of information inferred from such plots is valuable for guiding the overall design of the whole industrial application. It can be said that one would favour operations upstream of the biosorption process to carry lower temperature outputs and that there would be a trade-off between maintaining lower upstream temperatures and cooling efforts that might be required to increase the efficiency of the biosorption process. Quantified representation of such information aids the preliminary design calculations for the whole process and guides early design decisions.

Adsorption model	T (°C)	K_L	q_0	Adj-R^2	RMSE
Langmuir	25	0.526	2.690	0.725	0.286
	30	0.717	2.184	0.751	0.198
	35	0.924	1.796	0.830	0.114
	50	1.497	1.548	0.931	0.046

Adsorption model	T (°C)	K_F	n_F	Adj-R^2	RMSE
Freundlich	25	1.346	5.387	0.871	0.196
	30	1.234	6.328	0.849	0.154
	35	1.121	7.615	0.975	0.044
	50	1.128	11.063	0.888	0.058

Adsorption model	T (°C)	K_S	a_S	β_S	Adj-R^2	RMSE
Sips	25	1.752	0.406	0.376	0.827	0.227
	30	1.829	0.634	0.441	0.820	0.169
	35	1.804	0.721	0.355	0.992	0.024
	50	2.550	1.522	0.589	0.975	0.028

Adsorption model	T (°C)	K_{RP}	α_{RP}	β_{RP}	Adj-R^2	RMSE
Redlich-Peterson	25	9.713	6.637	0.836	0.813	0.236
	30	5.001	3.480	0.882	0.803	0.176
	35	5.689	4.525	0.898	0.992	0.025
	50	3.749	2.783	0.958	0.981	0.024

Adsorption model	T (°C)	b_K	q_0	n_K	Adj-R^2	RMSE
Khan	25	7.343	1.013	0.829	0.811	0.237
	30	3.411	1.201	0.876	0.801	0.177
	35	4.284	1.064	0.895	0.992	0.025
	50	2.717	1.277	0.956	0.982	0.023

Adsorption model	T (°C)	A_T	b_T	Adj-R^2	RMSE
Temkin	25	23.567	6386.6	0.878	0.191
	30	56.442	8814.2	0.872	0.142
	35	186.64	12536.0	0.992	0.024
	50	5066.8	20808.0	0.920	0.049

Table 3: Parameters and statistics of the fitted isotherm models.

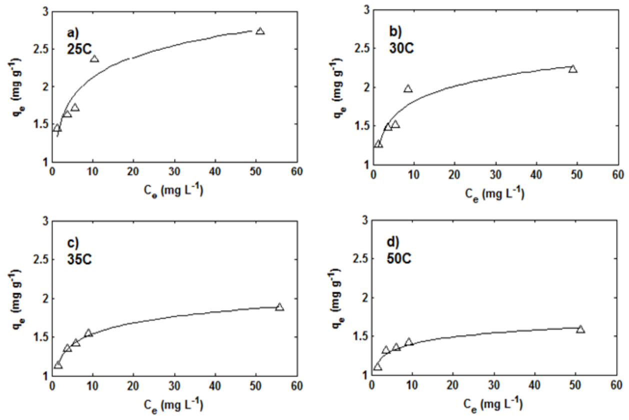

Figure 3: Effect of initial Co(II) concentration on the isothermal relationship between metal uptake and residual metal concentration at equilibrium with fitted Temkin isotherms (pH 5.0, biosorbent dose: 1.0 g L^{-1}, agitation rate: 150 rpm).

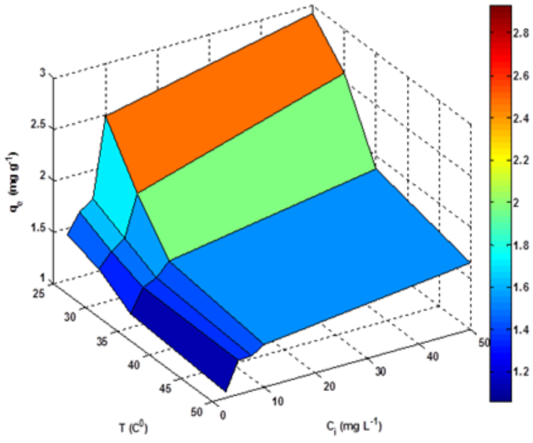

Figure 4: Combined effect of temperature and initial Co(II) concentration on biosorption by inactive *S. pombe*.

Biosorption kinetics

Determining the kinetics of a biosorption process is a key step towards reactor sizing and process optimisation. The rate of adsorption can be calculated by considering the biosorption process as a reaction system and assuming biosorbent concentration to be in great excess with respect to sorbent concentration. Following these assumptions biosorbate concentration can be grouped with the basic rate constant yielding a pseudo-constant which can be used in either a first or second order kinetic model. Both the pseudo-first and pseudo-second order approaches have been tested to correlate the present experimental data. Calculations were done using initial metal concentration values of 2.5, 5.0, 7.5, 10.0 and 50.0 mg L^{-1} at 25, 30, 35 and 50°C temperatures. It was found that pseudo-first order kinetics showed a better fit statistically. Optimised pseudo-first order rate constants with observed and calculated values for equilibrium metal uptake are reported in Table 4 along with statistical parameters.

Statistical analysis of the fit of kinetic data to pseudo-first and pseudo-second order models reveals marginally Better Square of correlation factors, R^2, for the former. A better fitting pseudo-first order kinetics might imply the absence of a chemical sorption mechanism between Co(II) and the cellular surface of *S. pombe* or its insignificance in comparison to physical interactions. It is also clear from equilibrium metal uptake values that the overall biosorption of Co(II) by *S. pombe* is not a very efficient process. These observations should be considered in an industrial application context, in terms of the reversibility of this operation and its potential use in a multi-component biosorption process.

Preliminary design calculations for a single stage biosorber

An important step towards the industrial design of a biosorption process is the utilisation of the characterisation data (biosorption isotherms) for the calculation of some relevant metrics [12]. The operating volume of a single stage operation is an important metric in terms of equipment design and operational costs. Determination of the biosorbent mass required achieving a target percentage removal for a given operating volume at a given pH and temperature is a design objective. The mass balance for Co(II) over a single stage of biosorption, depicted in Figure 5, at equilibrium is as follows:

$$V(C_i+[Spombe]_i q_i)=V(C_e+[Spombe]_e q_e) \qquad (5)$$

Assuming biosorbent amount doesn't change (i.e. $[Spombe]_i=[Spombe]_e$) throughout the process and substituting in the Temkin isotherm, the above equation yields: at equilibrium.

$$[Spombe]_i=\frac{C_i-C_e}{\frac{RT}{b_T}\ln A_T C_e} \qquad (6)$$

Figure 6 displays the amount of biosorbent needed to achieve predetermined percentage removal of metal in terms of varying operational volume. Although optimal biosorbent dose has been found to be 1.0 g L^{-1}, this optimality is in terms of the adsorption capacity of the biosorbent. If the cost of biosorbent is a critical factor for process design then this optimality is an important measure. However, if there is a trade-off between the cost of biosorbent and the cost of downstream operations then the kind of information gained from Figure 6 becomes important in guiding process design decisions.

T (°C)	C_i (mg L^{-1})	$q_{e\text{-}exp}$ (mg g^{-1})	Pseudo-first order model		
			k_{p1}	$q_{e\text{-}cal}$ (mg g^{-1})	R^2
25	2.790	1.437	2.501	1.413	0.9998
	5.511	1.630	2.167	1.633	0.9999
	7.440	1.724	1.712	1.725	0.9983
	12.813	2.367	0.563	2.542	0.9996
	53.716	2.728	0.187	2.997	0.9988
30	2.594	1.255	2.359	1.337	0.9999
	5.182	1.473	1.863	1.492	0.9998
	7.039	1.515	1.491	1.562	0.9933
	10.553	1.967	0.397	1.934	0.9925
	51.068	2.226	0.110	2.589	0.9942
35	2.603	1.131	1.891	1.141	0.9986
	5.088	1.355	1.557	1.361	0.9979
	7.407	1.416	1.219	1.381	0.9974
	10.528	1.544	0.283	1.564	0.9989
	57.600	1.878	0.046	1.852	0.9997
50	2.630	1.100	1.765	1.066	0.9988
	5.011	1.316	1.396	1.335	0.9934
	7.448	1.346	0.618	1.358	0.9968
	10.630	1.416	0.183	1.419	0.9975
	52.787	1.578	0.023	1.656	0.9981

Table 4: Pseudo-first order kinetic model.

Determination of thermodynamic properties

The pseudo-first order kinetic equilibrium constant can be utilised to calculate the activation energies for the predetermined experimental conditions using equation 2. Figure 7 shows the linearized ln k_{p1} versus reciprocal temperature plots for various initial sorbent concentration values. E_a values have been found to be -11.42, -13.53, -33.45, -34.88 and -66.48 kJ mol^{-1} for initial metal concentrations of 2.5, 5.0, 7.5, 10.0 and 50.0 mg L^{-1}, respectively. Negative nature of the activation energy values suggest that biosorption of Co(II) onto *S. pombe* is barrierless in these concentration ranges but no further physical interpretation is possible expect that the process is exothermic. This is an advantageous feature as it implies a low-cost operation with lower energy requirements, quick recovery and minimal loss of efficiency when compared to endothermic operations.

Further thermodynamic properties of the biosorption system were determined using equations 3 and 4. The calculated values for ΔS° and ΔH° are reported in Figure 8. The equilibrium constant from the Freundlich isotherm model was used for the thermodynamic calculations although statistically the Temkin isotherm was a better fit, albeit marginally. The reason for this is the thermodynamic consistency the calculations with the Freundlich equilibrium constants provide which is lacking in the Temkin calculation.

It can be observed from Figure 9 that increasing the operating temperature of the biosorption process has detrimental effects on two critical process metrics, namely the time required to reach equilibrium and metal uptake at equilibrium. Accordingly, it can be argued that, in terms of recovery of the metal from solution, temperature increase makes this process less favourable. Thermodynamic interpretation of such a biosorption process with above-mentioned features suggests that the Δ*G*° of the process should increase with increasing operating temperature. Thermodynamic properties calculated using the equilibrium constants acquired from the fitting of experimental data to biosorption isotherms produce trends that suggest otherwise with the exception of Freundlich and Redlich-Peterson models which exhibit acceptable thermodynamic consistency. Thermodynamically inconsistent predictions are expectable since these isotherm models are highly empirical and lack physical meaning; even though they offer statistically very accurate representation of equilibrium data [10,13]. Following these considerations, for the calculation of thermodynamic parameters, the equilibrium constant from the thermodynamically consistent isotherm model rather than the statistically most successful one will be used; as long as the former carries an acceptable correlation factor. Different trends depending on the isotherm model use can be observed in the calculated values of Δ*G*^{0} as reported in Table 5.

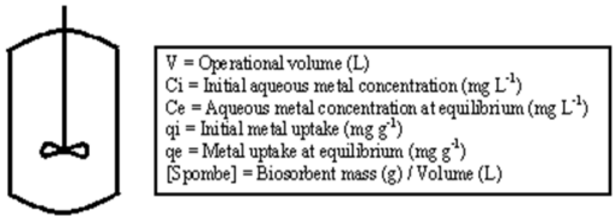

Figure 5: Batch biosorber.

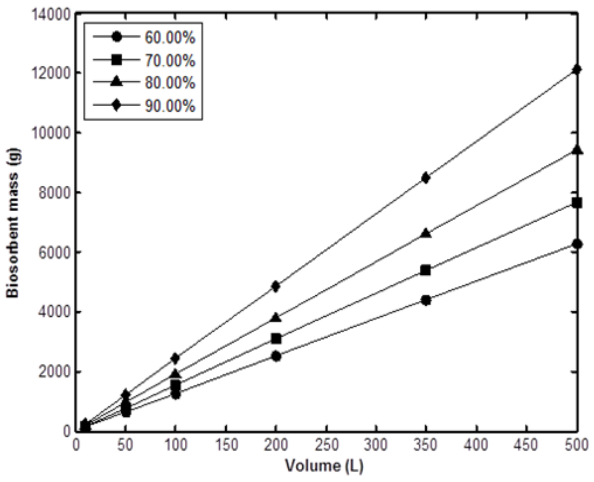

Figure 6: Biosorbent mass required for target percentage removal of metal at various operating volumes @ 25oC.

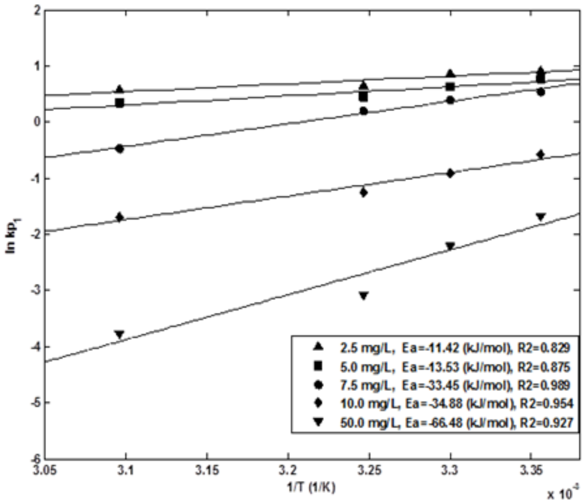

Figure 7: ln k_{p1} versus 1/T plots at different initial Co(II) concentrations.

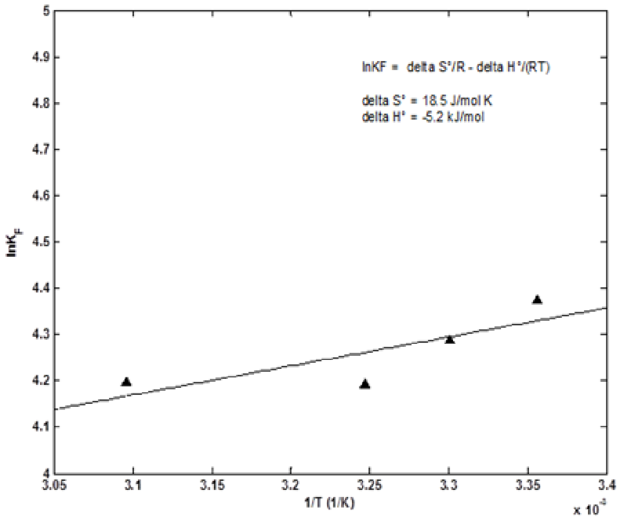

Figure 8: ln K_F versus 1/T plot.

Conclusion

Equilibrium, kinetic and thermodynamic analyses of a biosorption process are crucial for predicting its performance and comparison with alternatives. Among the various studied isotherm models, Temkin isotherm model has shown the best fit for the present data in terms of statistical success. The inclusion of a term for temperature in its mathematical structure and the experimentally observed fact that temperature has an inversely correlated effect on biosorption performance support this outcome. However, thermodynamic consistency with experimental observations in the calculation of thermodynamic properties of the system could only be achieved using equilibrium constants from the Freundlich isotherm model. This proves to be a situation where one has to choose the most appropriate model for the type of calculation needed. Indeed, equilibrium studies were conducted using the Temkin isotherm model whereas thermodynamic calculations were done incorporating the Freundlich equilibrium constant.

The ΔG^0 values calculated for operating temperatures of 25, 30, 35 and 50°C were -11.7, -11.5, -11.3 and -11.3 kJ mol^{-1}, respectively. The slight increase in the ΔG^0 values with respect to increasing operating temperatures implies thermodynamic consistency with the observation from kinetic profiling simulations (Figure 9) that higher temperatures are less favourable for this particular system.

Among the isotherm models used only Temkin isotherm takes the natural logarithm of aqueous metal concentration whereas all the others incorporate this term either linearly or exponentially. Temkin isotherm seems to minimise the effect of aqueous metal concentration on equilibrium compared to all the other models. It has to be noted that this is in parallel with experimental observation. Although increased initial metal concentrations have a positive effect on the equilibrium values of q_e and C_e, this is a marginal effect and insignificant with that of other factors such as temperature. The success of the Temkin isotherm model may be due to its reflecting this fact.

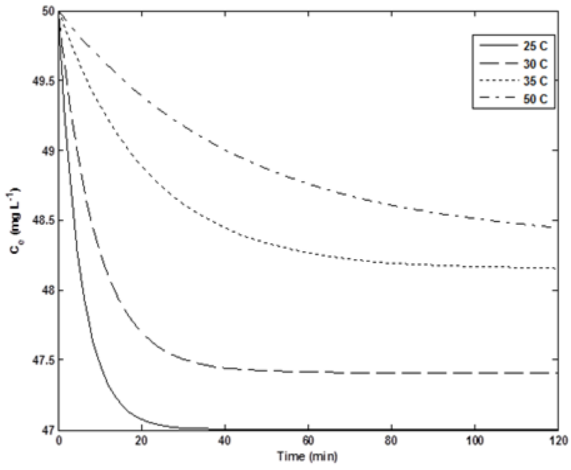

Figure 9: Kinetic profiling simulation of four biosorption processes taking place at different operating temperatures all with C_i=50 mg L^{-1} and biosorbent dose: 1 g L^{-1}.

	ΔG^0@ 25°C (kJ mol^{-1})	ΔG^0@ 30°C (kJ mol^{-1})	ΔG^0@ 35°C (kJ mol^{-1})	ΔG^0 @ 50°C (kJ mol^{-1})
Langmuir	-8.5	-9.4	-10.2	-12.0
Freundlich	-11.7	-11.5	-11.3	-11.3
Sips	-11.0	-11.3	-12.0	-13.5
Khan	-16.3	-14.2	-14.9	-13.6
Temkin	-35.0	-37.8	-41.5	-52.4
Redlich-Peterson	-16.0	-14.3	-15.0	-14.5

Table 5: ΔG^0 values calculated using equilibrium constants from different isotherm models.

The above observation is supported by the outcome of the biosorption kinetics study as well. Pseudo-first order kinetics provides a statistically superior correlation of experimental data compared to the pseudo-second order kinetics. The mathematical difference between the two is the taking of the square of the concentration term in the pseudo-second order kinetics increasing its influence on the overall kinetic behaviour of the biosorption system. The fact that pseudo-first order kinetics better describes the observed values is in agreement with the earlier suggestion. The fact that this biosorption system follows pseudo-first order kinetics hints that a costly destructive desorption step might not be necessary in order to free the biosorbent for reuse.

It is important to integrate biosorbent characterisation information with preliminary process design calculations from an early point onwards. The use of isotherm models to simulate the single stage biosorber performance plots (Figure 6) and the subsequent identification of possible techno-economic trade-off points can be considered a tool for early stage process design.

Overall, the biosorption of Co(II) by wild-type *S. pombe* seems to be a slightly exothermic process, judging by the negative nature of the calculated E_a values and thermodynamically feasible, considering that the calculated ΔG^0 values are negative for all the conditions tested. However, this particular biosorption process is not a very efficient one since a maximum of about 50% percentage removal of metal is possible even under optimal conditions. This value is obtained when lower initial metal concentrations are used. For higher initial metal concentrations the percentage removal falls dramatically to under 20% for 10 mg L^{-1} initial Co(II) concentration and ~5% for 50 mg L^{-1} initial Co(II) operations. This means that while *S. pombe* is not an ideal biosorbent for the removal of Co(II) from aqueous solutions, it can be utilised as a bioseparation agent for aqueous mixtures containing both Ni(II) and Co(II) since its affinity towards Ni(II) is significantly higher (Durmaz-Sam et al., 2011).

Future work could focus on the characterisation of *S. pombe* in multi-component biosorption processes involving both Co(II) and Ni(II). Additionally, alternative design considerations for better utilisation of *S. pombe*, such as the use of column systems instead of a batch stirred tank reactor or the immobilisation of *S. pombe* could be studied. Inclusion of mass transfer and fluid-flow calculations would improve the preliminary design approaches. Finally, quantified techno-economic assessment of the design trade-offs using cost-benefit analyses would enhance the industrial feasibility studies.

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References

1. Wang J, Chen C (2009) Biosorbents for heavy metal removal and their future. Biotechnol Adv 27: 195-226.
2. Durmaz-Sam S, Sayar NA, Topal-Sarikaya A, Sayar AA (2011) Biosorption of Ni(II) by *Schizosaccharomyces pombe:* kinetic and thermodynamic studies. Bioprocess Biosys Eng 35: 997-1005.
3. Kuyucak N, Volesky B (1989) Accumulation of cobalt by marine algae. Biotechnol Bioeng 33: 809-814.

4. Vijaraghavan K, Palanivelu K, Velan M (2006) Biosorption of copper(II) and cobalt(II) from aqueous solutions by crab shell particles. J Hazard Mater 97: 1411-1419.
5. Pal A, Ghosh S, Paul A (2006) Biosorption of cobalt by fungi from serpentine soil of Andaman. Bioresource Technol 97: 1253-1258.
6. Li B, Liu F, Wang J, Ling C, Li L, et al. (2012) Efficient separation and high selectivity for nickel from cobalt-solution by a novel chelatin resin: batch, column and competition investigation. Chem Eng J 195-196: 31-39.
7. Kumbasar RA, Sahin I (2008) Separation and concentration of cobalt from ammoniacal solutions containing cobalt and nickel by emulsion liquid membranes using 5,6-dibromo-8-hydroxyquinoline (DBHQ). J Membrane Sci 325: 712-718.
8. Ozer A, Ozer D (2003) Comparative study of biosorption of Pb(II), Ni(II) and Cr(IV) ions onto *S. ceravisiae*: determination of biosorption heats. J Hazard Mater 100: 219-229.
9. Volesky B (2003) Bioprocess process simulation tools. Hydrometallurgy 71: 179-190.
10. Liu Y, Liu YJ (2008) Biosorption isotherms, kinetics and thermodynamics. Sep Purif Technol 61: 229-242.
11. Foo KY, Hameed BK (2010) Insight into the modelling of adsorption isotherm systems. Chem Eng J 156: 2-10.
12. Hameed BH, Mahmoud DK, Ahmad AL (2008) Equilibrium modelling and kinetic studies on the adsorption of basic dye by a low-cost adsorbent: Coconut (Cocos nucifera) bunch waste. J Hazard Mater 158: 65-72.
13. Levan MD, Vermeulen T (1981) Binary Langmuir and Freundlich isotherms for ideal adsorbed solutions. J Phys Chem-Us 85: 3247-3250.