

## Thermodynamic Characterization of Copper Biosorption Process by pretreated *A. niger* Biomass

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### Abstract

Thermodynamic equations are developed for biosorption of copper in pretreated *A. niger* biomass based on the concept of solution thermodynamics. The integral and differential thermodynamic equations for different thermodynamic functions like Gibbs free energy, enthalpy, entropy, needed for characterization of biomass for engineering calculations is also presented. The metal – biomass system has been tested at different temperature. The enthalpy change of biosorption of copper process has been evaluated by using van't Hoff equation related to the energy of sorption. The thermodynamics of copper ion in pretreated *Aspergillus niger* biomass system indicates spontaneous and exothermic nature of the process.

**Keyword:** Thermodynamics, Characterization, Biomass, Temperature, Sorption.

### Introduction

Biosorption has come up as an alternative method for removal of heavy metals from wastewater. Among other metals, removal of copper by biosorption from wastewater is of interest in recent days. Batch kinetic study for the copper removal by pretreated *A. niger* is useful for effectiveness of copper biomass system [1]. The nature of the sorbing surface is the determining factor in sorption. Surfaces of the prepared biomass are irregular at the molecular level with appropriate sites for metal complexation [2]. Two possibilities are there, one is if the sites are close together the adsorbed copper may interact with one another or if they are sufficiently dispersed, the adsorbed molecules may interact only with the sites. Though the main focus has been given to the physical and chemical characterization and kinetic and equilibrium study, thermodynamic characterization has been given little or no importance. The study of copper *A. niger* interactions at thermodynamic level is required from theoretical basis. Either Langmuir constant or Gibbs free energy equation has generally given the focus to the temperature dependence of the fungal biomass and evaluation of the enthalpy change of biosorption process.

In the biosorption process the overall enthalpy of the interactions is non-zero, so a temperature dependence of metal ion biosorption by microorganisms will occur [3]. Temperature changes will affect factors like the stability of the metal ion species initially placed in solution, the stability of the metal–fungi complex depending on the biosorption sites, the cell wall configuration and the ionization of the reactive groups on the fungus cell [4].

Sag [3] reported that the thermodynamic parameters like enthalpy change of the biosorption of Cu (II) and Ni (II) ion on *Z. ramigera* and *R. arrhizus* are exothermic and sharply affected by temperature rise and maximum reached at 25 °C. The initial biosorption rates for Pb (II), Cr (II), and Fe (III) ions increased with increasing temperatures in the range 15-45 °C [5][6][7]. The binding of Cr (VI) by *S. equisimilis*, *S. cerevisiae* and *A. niger* indicates that the process was endothermic in nature i.e. temperature rise in the incubator increased the biosorption rates [8].

In this paper the thermodynamics of biosorption of Copper (II) in pretreated *Aspergillus niger* biomass are investigated. To understand the copper- *A. niger* interactions from first principle of integral and differential thermodynamic equations are used [9] for thermodynamic characterization of the biomass. Different thermodynamic functions like Gibbs free energy, enthalpy, entropy, needed for characterization of biomass, are established based on solution thermodynamics concept. Copper sorption equilibrium over a temperature range of 33 – 45 °C is studied and the enthalpy change for the biosorption process is evaluated based on van't Hoff equation.

## Materials and Methods

### Growth of Culture

The fungus *Aspergillus niger* strain NCIM 618 (ATCC 10594), was obtained from NCIM, Pune, India and used for the sorption. The laboratory strain of *A. niger* was propagated in potato dextrose agar (PDA) consisting of 39g/l Himedia PDA and 0.1 g/l of yeast extract. The culture was maintained in slants and was incubated for 5-7 days at 33 ± 2 °C. Fungal biomass was cultivated in liquid medium using the shake flask method. The growth medium used had the following composition (g/l): dextrose, 30; peptone 10; (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, 0.4; KH<sub>2</sub>PO<sub>4</sub>, 0.2; MgSO<sub>4</sub>, 7H<sub>2</sub>O, 0.2. All reagents were from Himedia or Merck (Mumbai, India). The pH of the growth medium was adjusted to 5.8-6.0 by the addition of 0.1 N HCl prior to autoclaving. Once inoculated, flasks were shaken on a rotary shaker at 200 rpm for five days at 33 ± 2 °C. The culture was grown as discrete pellicles. After harvest the biomass was transferred to a 1% formalin solution for 24 hrs. The biomass was then dried at 60 °C for 20-24 hrs and powdered in a mortar. The powdered biomass residue was used for further studies.

### Instrumentation

The surface functional groups were characterized by FTIR (Magna 550, USA). Copper concentrations were measured by atomic absorption spectroscopy (AAS-SL 173, EIL).

### Influence of Temperature

The effect of temperature of exposure of the biomass powder to metals on the biosorption characteristics was investigated. Metal solution at 50 mg/l was prepared by dissolving copper metal in conc. HNO<sub>3</sub> in double distilled water. The thermodynamic experiments were studied over a temperature range of 33 – 45 °C at pH 6.0 with 0.002 g/ml of biomass and continuous stirring at 200 rpm for 3 hrs. At the indicated times aliquots of the

liquid phase were withdrawn and used to determine the amount of metal remaining in solution. All experiments were performed in triplicate and the average value was taken for analysis.

### Thermodynamic Characterization of the Biomass

The fundamental equations for energy, enthalpy and free energy of the biosorption of copper (II) by the pretreated *Aspergillus niger* is investigated. Sorption of copper (II) in the prepared biomass can be explained with the help of solution thermodynamics, with the only difference, the solvent is solid [10]. Assuming that the particle size distribution, composition and structure of the prepared biomass are uniform throughout the system, equations in Table 1 gives the fundamental thermodynamic property relation of the raw and sorbed biomass together with the adsorbed phase.

Biosorption process can be operated either in continuous in packed column or sample cell containing a fixed mass of biomass (batch operation). The biomass (solid phase) is open with respect to the copper solution, but closed with respect to the biomass itself. The reversible addition of biomass to the system is not physically possible and the mass of biomass is constant. The assumptions considered to present the basic thermodynamic equations of the biomass- metal system are as follows. (i) The biomass is incompressible; (ii) the enthalpy is equal to the internal energy, because the volume of the adsorbed phase is zero; (iii) the Helmholtz free energies and Gibbs free energies are equal for the same reason.

The free energy of the adsorbed phase consists of the free energy of  $n_c^a$  mols of metal species in the equilibrium state and the surface potential ( $\phi$ ), which is zero if no adsorption takes place. The chemical potential of the biomass varies with the isothermal loading of the metal ions. In molecular simulation, it is generally assumed that the adsorbent generates an invariant potential field. Due to the existence of the potential field free energy changes which consists of both energetic and entropic contributions. From the solution thermodynamics point of view the contact of the adsorbate molecules with the atoms of the adsorbent material alters the chemical potential of the solid. In the case of metal sorption in the prepared biomass at constant temperature and pressure only intensive variable capable of change is the chemical potential of the biomass.

### Surface Potential

The surface potential, which is the chemical potential of the sorbed biomass relative to the raw biomass, is expressed by equation 1-3.

$$\phi = G^a - \mu_c n_c^a \dots\dots\dots(1)$$

Differentiating and rearranging and using the assumptions,

$$d\phi = -S^a dT + n_c^a d\mu_c \dots\dots\dots(2)$$

This is one form of Gibbs–Duhem relation. At constant temperature this equation reduces to the Gibbs adsorption isotherm as in equation 3.

$$d\phi = n_c^a d\mu_c \dots \dots \dots (3)$$

The surface potential is a state function so the integration for  $\phi$  is independent of the path. Applying the solution thermodynamics concept and the  $\Delta G$  value from experiment chemical potential of the biomass can be determined indirectly by integrating the chemical potential of the metal ion.

## Results and Discussions

### Influence of Temperature

Free energy a property of the system decrease of which was a measure of the external work available during the transformation of the system. The change in free energy ( $\Delta G^a$ ) varies considerably with temperature. The temperature range used in this study was from 33 °C to 45 °C. The sorption decreases with temperature. Thermodynamic parameters such as free energy change ( $\Delta G^a$ ) and enthalpy change ( $\Delta H^a$ ) of biosorption were determined using the following equations [11]. For the sorption of metal ion on the biomass in aqueous solution,

$$K_e = \frac{C_{Ae}}{C_e} \dots \dots \dots (4)$$

where  $K_e$  is equilibrium constant and  $C_{Ae}$  and  $C_e$  are the equilibrium concentration (mg/l) of the metal ion on the biomass and in the solution respectively.

Now, assuming that at the reaction condition all the reactants and the resultants are in standard state then the correlation between the free energy change and the equilibrium constant of the process can be written as equation 5.

$$\Delta G^a = -RT \ln K_e \dots \dots \dots (5)$$

where T is temperature in Kelvin and R is the gas constant. The quantitative expression for the variation of equilibrium constant with temperature is known as van't Hoff equation and can be written in the integrated form as equation 6.

$$\ln K_e = -\frac{\Delta H^a}{RT} + C \dots \dots \dots (6)$$

As shown in figure1, assuming  $\Delta H^a$  as constant was obtained from the slope of van't Hoff plots of  $\log K_e$  vs.  $1/T \times 10^3$  in K.

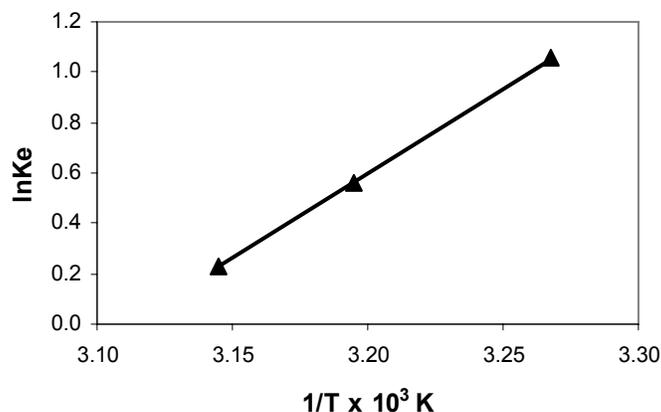
**Table 1:** Thermodynamic properties of raw and sorbed biomass and the solution phase.

		Sorbed Biomass	Raw Biomass	Adsorbed Phase
Internal Energy, U	Integral	$U^m = TS^m - PV^m + \mu_c n_c + \mu$	$U^p = TS^p - PV^p + \mu^p$	$U^a = U^m - U^p$
	Diff.	$dU^m = TdS^m + \mu dn_c$	$dU^p = TdS^p$	$U^a = TS^a + \mu_c n_c^a + \phi$ $dU^a = TdS^a + \mu_c dn_c^a$
Entropy, S	Integral	$S^m$	$S^p$	$S^a = S^m - S^p$
	Diff.	$dS^m$	$dS^p$	$dS^a = dS^m - dS^p$
Volume, V	Integral	$V^m$	$V^p$	$V^a = V^m - V^p = 0$
	Diff.	$dV^m$	$dV^p$	$dV^a = dV^m - dV^p = 0$
Moles, n	Integral	$n_c^m$	—	$n_c^a = n_c^m$
	Diff.	$dn_c^m$	—	$dn_c^a = dn_c^m$
Helmholtz free energy, A	Integral	$A^m = U^m - TS^m$	$A^p = U^p - TS^p$	$A^a = \mu_c n_c^a + \phi$
	Diff.	$dA^m = dU^m - TdS^m$	$dA^p = dU^p - TdS^p$	$dA^a = \mu_c dn_c^a$
Gibbs free energy, G	Integral	$G^m = A^m + PV^m$	$G^p = A^p + PV^p$	$G^a = \mu_c n_c^a + \phi$
	Diff.	$dG^m = dA^m + PdV^m$	$dG^p = dA^p + PdV^p$	$dG^a = \mu_c dn_c^a$
Enthalpy, H	Integral	$H^m = U^m + PV^m$	$H^p = U^p + PV^p$	$H^a = TS^a + \mu_c n_c^a + \phi$
	Diff.	$dH^m = dU^m + PdV^m$	$dH^p = dU^p + PdV^p$	$dH^a = dS^a + \mu_c dn_c^a$

**Table 2:** Equilibrium constant, enthalpy and Gibbs free energy at different temperature

Temperature in °K	Ke	$\Delta H^a$	$\Delta G^a$
306	2.859	-55.52	-2.682
313	1.758		-1.469
318	1.260		-0.610

Negative values of  $\Delta H^a$  as listed in table 2 suggested the exothermic nature of adsorption. The negative values of  $\Delta G^a$  indicate spontaneous nature of adsorption of Copper (II) on the biomass.



**Figure 1:** A van't Hoff plot of  $\log K_e$  vs.  $1/T \times 10^3$  in  $^\circ\text{K}$ .

### Conclusion

The development of the fundamental thermodynamic equations for the characterization of the solid biomass has not been given proper attention in the literature. In this study a systematic integral and differential equations of the thermodynamic parameters like Gibbs free energy, enthalpy, surface potential of the formalin washed *Aspergillus niger* biomass has been developed using the concept from the first principle of solution thermodynamics. The temperature dependence of the biosorption of Cu (II) evaluated from the van't Hoff equation and it indicates spontaneous and exothermic reaction.

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### Nomenclature

T	Temperature
P	Pressure
$\mu_c$	Chemical potentials of the copper (II) in J/mol
$\mu$	Chemical potential of the sorbed biomass in J/kg
U	Internal energy of the biomass
S	Entropy of the biomass
V	Volume of the biomass
A	Helmholtz free energy of the biomass
G	Gibbs free energy of the biomass
H	Enthalpy of the biomass
$n_c$	Number of moles of copper (II) in sorbed biomass
m	Mass of solid biomass
$U^m$	Internal energy per unit mass of biomass
$S^m$	Entropy per unit mass of biomass
$V^m$	Volume per unit mass of biomass
$n_c^m$	Number of moles of copper (II) per unit mass of biomass
$U^p$	Internal energy of biomass at standard state
$S^p$	Entropy of the biomass at standard state
$V^p$	Volume of the biomass at standard state
$\mu^p$	Chemical potential of the raw biomass at standard state

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### Nomenclature

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$U^a$	Internal energy of adsorbed phase (copper (II))
$S^a$	Entropy of adsorbed phase (copper (II))
$V^a$	Volume of adsorbed phase (copper (II))
$n_a$	Number of moles of copper (II) in adsorbed phase
$\phi$	Surface potential
$A^a$	Helmholtz free energy of adsorbed phase (copper (II))
$G^a$	Gibbs free energy of adsorbed phase (copper (II))
$H^a$	Enthalpy of adsorbed phase (copper (II))

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