



# Kinetics and equilibrium studies on removal of zinc(II) by untreated and anionic surfactant treated dead biomass of yeast: Batch and column mode

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## ABSTRACT

The present study was carried out using dead biomass of isolated yeast species viz. *Candida rugosa* and *Candida laurentii* as biosorbents for the removal of Zn(II) from aqueous environment. *C. rugosa* and *C. laurentii* exhibited 65.4% and 54.8% removal of zinc at pH 6.0 in presence of 90 mg L<sup>-1</sup> Zn(II) at 30 °C in batch system. Remarkable increase in Zn(II) removal was noted using dead yeast biomass treated with anionic surfactant sodium dodecyl sulphate (SDS) which was confirmed through SEM analysis. Kinetic studies based on various models were carried out and the results showed a very good compliance with the fractional power model. The experimental data were analyzed using two, three and four parameter isotherm models. The most appropriate equation for describing the isotherm profile was Freundlich model. The biosorbent performance was evaluated in column mode packed with SDS treated dead biomass of *C. rugosa* entrapped in sodium alginate beads. FT-IR analysis showed the involvement of –NH, –C=O and –COOH functional groups in the binding of Zn(II) by yeast. The present study confirmed that immobilized SDS treated dead biomass of *C. rugosa* may serve as potential and eco-friendly biosorbent for removal of Zn(II) ions from aqueous solution.

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## 1. Introduction

Zinc is an essential element required for growth and metabolism of living organisms, but it may be toxic when its concentration exceeds that required for correct biological functioning [1]. In the Dangerous Substances Directive (76/464/EEC) of the European Union, zinc has been registered as List 2 Dangerous substance with the Environmental Quality Standards being set at 40 µg L<sup>-1</sup> for estuaries and marine waters and at 45–500 µg L<sup>-1</sup> for fresh water depending on water hardness [2]. Zinc is phytotoxic, and the recommended level of zinc for disposal on agricultural land is 2.5 mg g<sup>-1</sup> of dried sludge solids. The maximum permissible limit for its concentration in effluent discharged into natural water bodies is 5 mg L<sup>-1</sup> [3].

Zinc is often found in high concentrations in the effluents discharged from industries such as manufacture of alloys, sheet metal galvanization, TV picture tubes etc. Discharging these effluents into natural systems adjoining landmasses and sewer systems is a normal practice in small and medium scale industries. This poses serious problems to the environment and ecosystems. The World Health Organization (WHO) recommends a 5.0 mg L<sup>-1</sup> maximum acceptable concentration of zinc in drinking water [4].

Consequently, there is a significant interest regarding zinc removal from wastewater [5].

Conventional methods for metal removal include precipitation, filtration, coagulation, evaporation, ion exchange, membrane separation and solvent extraction. However, application of such processes is always expensive and ineffective in terms of energy and chemical products consumption, especially at low concentrations of 1–100 mg L<sup>-1</sup>. Biosorption is considered as promising technology in the removal of metal ions from aqueous solutions in water pollution control [6]. A number of studies have evaluated the application of biosorption technique for the removal of Zn(II) using microorganisms such as bacteria [7–11], fungi [12–14] and yeast [15,16] but reports on equilibrium studies on biosorption of zinc(II) is scanty which is most important in understanding the biosorption process.

Many biosorbents do not exhibit their full potential in the raw (untreated) form and their metal uptake capacity has been found to improve significantly upon chemical pre-treatment [17,18]. Pre-treatment methodology using caustic-treated immobilized yeast have been reported and evaluated for improving the zinc uptake potential of biosorbent [19]. As caustic treatment of biomass can result in solubilization and subsequent loss of biomass during metal binding process [20], use of anionic surfactant SDS for pre-treatment may be a better choice towards removal of zinc from aqueous environment. Surfactant molecules can reduce surface and interfacial tensions in aqueous phase [21]. So, in the present study

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### Nomenclature

$q_m$	maximum sorption capacity ( $\text{mg g}^{-1}$ )
$q_e$	amount of adsorbate adsorbed at equilibrium ( $\text{mg g}^{-1}$ )
$q_{m0}$	the maximum adsorption capacity ( $\text{mg g}^{-1}$ ) in the Baudu isotherm equation
$q_{mLF}$	the Langmuir–Freundlich maximum adsorption capacity ( $\text{mg g}^{-1}$ )
$q_t$	amount of sorbate sorbed at time $t$ ( $\text{mg g}^{-1}$ )
$r^2$	Correlation coefficient
$r_R$	Radke–Prausnitz model constant
$R$	universal gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
$R_L$	Langmuir separation factor
RMSE	root mean square error
S.E.	standard error
SSE	sum of squares error
$T$	time (min)
$\nu$	fractional power model constant
$V$	volume of metal solution (L)
$W$	mass of sorbent (g)
$x$	the Baudu isotherm parameter
$y$	the Baudu isotherm parameter
<i>Greek symbols</i>	
$\alpha_E$	initial sorption rate in Elovich model ( $\text{mg g}^{-1} \text{ min}^{-1}$ )
$\beta_E$	desorption constant in Elovich model ( $\text{g mg}^{-1}$ )
$\alpha$	exponent in the Fritz–Schlunder model that lies between 0 and 1
$\beta$	exponent in the Fritz–Schlunder model that lies between 0 and 1

the possible use of dead yeast biomass treated with anionic surfactant, sodium dodecyl sulphate (SDS) have been investigated to improve the zinc adsorption potential.

The use of microbial biomass in freely suspended state is limited owing to their inherent disadvantages. Immobilized biomass offers greater potential applications with benefit [22–24]. The choice of immobilization matrix is a key factor in environmental application of immobilized biomass. Use of alginate has many advantages including ease of use, cheap, good shelf life, non toxic, good surface detail and setting time can be controlled with temperature of water used [25].

In practice, continuous flow operations in column mode are more useful than batch mode for large scale wastewater treatment. However, little effort has been focused on employing column packed with immobilized yeast for removal of zinc from synthetic solutions.

The aim of the present work was to study the sorption kinetics and biosorption equilibrium employing different isotherm models for the removal of Zn(II) by untreated and SDS treated dead biomass of yeast. Fourier transform infrared (FT-IR) analysis were used to study the potential binding sites and possible functional groups involved during zinc removal. Column studies were conducted using sodium alginate immobilized dead biomass of *C. rugosa* treated with SDS. The experimental data obtained were fitted to BDST model in order to predict the breakthrough curve of an adsorption process in a packed bed column. Regeneration experiments were also conducted to explore the possibility of reuse of the biosorbent.

## 2. Materials and methods

### 2.1. Biosorbent preparation

Two yeast species viz. *C. rugosa* and *C. laurentii* were isolated from Common Effluent Treatment Plant (CETP), Ranipet, Vellore, Tamilnadu, India. The yeasts were phenotypically characterised and identified to a species level by VITEK 2 Compact Yeast card reader with software version V2C 03.01 at the Council for Food Research and Development (CFRD), Kerala, India. The isolates were maintained in yeast extract peptone dextrose (YEPD) agar slants at  $4^\circ\text{C}$ . Mass cultivation of yeast isolates were carried out in inexpensive sugarcane bagasse extract medium as reported in our previous study [26]. The yeast biomass was harvested by centrifugation at 10,000 rpm for 5 min and subjected to drying at  $60^\circ\text{C}$  until a constant weight of biomass was obtained. Finely powdered dried yeast biomass was used for biosorption studies.

### 2.2. Metal solution preparation

Zinc(II) stock solution was prepared ( $1000 \text{ mg L}^{-1}$ ) by dissolving 4.55 g of powdered  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Hi Media, Mumbai, India) in 1000 mL of deionised water. The working solutions of metal were prepared by diluting the stock solution to the desired concentrations.

### 2.3. Batch mode biosorption studies

The effect of pH (3.0–9.0), sorbent dosage ( $0.5$ – $2.5 \text{ g L}^{-1}$ ), initial metal concentration ( $10$ – $110 \text{ mg L}^{-1}$ ) and contact time (10–360 min) on removal of zinc was investigated. The experiments were optimized at the desired pH, metal concentration, sorbent dosage and contact time using 100 mL of Zn(II) test solution in 250 mL Erlenmeyer flask. All the experiments were conducted at a constant temperature  $30^\circ\text{C}$ .

### 2.4. Analysis of zinc

Different concentrations of Zn(II) solutions were prepared by appropriate dilution from Zn(II) stock solution. The pH was adjusted using 0.1N HCl or 0.1N NaOH, respectively. Desired dosage of biomass was then added and the contents in the flask were shaken for the desired contact time in a shaker at required agitation time 120 rpm. At the end of agitation time, the samples were withdrawn and subjected to centrifugation at 10,000 rpm for 5 min. The residual concentrations of the supernatants were determined by Atomic absorption Spectrophotometer (Varian AA-240, Australia). Negative controls (without sorbents) were carried out to ensure that sorption was only by dried biomass of yeast species viz. *C. rugosa* and *C. laurentii*. The Zn(II) removal percentage using yeast as biosorbent was calculated from the expression:

$$\text{Zn(II) removal\%} = \frac{C_0 - C_f}{C_0} \times 100 \quad (1)$$

where  $C_0$  is the initial concentration of metal ( $\text{mg L}^{-1}$ ).  $C_f$  is the final concentration of metal ( $\text{mg L}^{-1}$ ). The amount of Zn(II) ion adsorbed onto yeast species were obtained by using the following expression Eq. (2),

$$q = \frac{C_0 - C_f}{M} \times V \quad (2)$$

where  $q$  is the sorption capacity i.e. the amount of Zn(II) ion biosorbed onto unit amount of biomass ( $\text{mg g}^{-1}$ );  $C_0$  and  $C_f$  are the concentrations ( $\text{mg L}^{-1}$ ) of the Zn(II) ion in the initial solution and after biosorption, respectively;  $V$  is the volume of the aqueous phase (l); and  $M$  is the amount of the biomass.

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