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Biosorption optimization of lead(II), cadmium(II) and copper(II) using response surface methodology and applicability in isotherms and thermodynamics modeling

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ABSTRACT

The present study was carried out to optimize the various environmental conditions for biosorption of Pb(II), Cd(II) and Cu(II) by investigating as a function of the initial metal ion concentration, temperature, biosorbent loading and pH using *Trichoderma viride* as adsorbent. Biosorption of ions from aqueous solution was optimized in a batch system using response surface methodology. The values of R^2 0.9716, 0.9699 and 0.9982 for Pb(II), Cd(II) and Cu(II) ions, respectively, indicated the validity of the model. The thermodynamic properties ΔG°, ΔH°, ΔE° and ΔS° by the metal ions for biosorption were analyzed using the equilibrium constant value obtained from experimental data at different temperatures. The results showed that biosorption of Pb(II) ions by *T. viride* adsorbent is more endothermic and spontaneous. The study was attempted to offer a better understating of representative biosorption isotherms and thermodynamics with special focuses on binding mechanism for biosorption using the FTIR spectroscopy.

1. Introduction

A world wide environmental problem has been invited over the past few decades due to tremendous increase in the metallic contents in the environment. Heavy metals are the main group of inorganic contaminants, and a considerable large area of land is contaminated with them due to use of sludge, pesticides, fertilizers, and emissions from municipal waste incinerators, car exhausts, residues from metalliferous mines, and smelting industries [1,2]. The industrial effluents discharge containing toxics heavy metals drain into the river, a source of drinking water for downstream towns. Wastewater treatment facilities in most of the developing countries are not well equipped to remove traces of heavy metals, thus exposing every consumer to unknown quantities of pollutants in the water they consume. Biosorption is a process that utilizes low cost biosorbents to sequester toxic heavy metals [3]. Biological treatment of wastewater is an innovative technology available for heavy metal remediation. Biosorbents such as algae, fungi and bacteria are examples of biomass tested for biosorption of several metals species with very encouraging results and are known to tolerate and accumulate heavy metals. To overcome the disadvantages toxic effect at elevated toxicant concentrations on living biomass; non-viable or dead biomass is preferred [4]. Among the microorganisms, fungal biomass seems to be a good sorption material, because, it can be produced easily and economically using simple fermentation techniques with a high yield of biomass and economical growth media [5]. Potential of filamentous fungi in bioremediation of heavy metal containing industrial effluents and wastewaters has been increasingly reported from different parts of the world [6]. However, filamentous fungi of heavy metals polluted habitat in India are not largely screened and exploited for their bioremediation potential. The advantages of biosorption over the conventional methods are low operating cost, selectivity for specific metal, short operational time and no chemical sludge [7]. It is necessary to submit a controlled application, either living or nonliving microbial cells under most influencing conditions, such as pH, temperature, sorbent mass and ionic concentration [8]. The response surface methodology successfully applied for the optimization of process variables indicated that it is a decision making tool. The main goal of the study was to investigate metals ions removal efficiency of the enveloping *Trichoderma viride* as a cost effective biosorbent using response surface methodology.

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Table 1
Process variables and their level.

Factors	Name	Units	Low actual	High actual	Low coded	Middle coded	High coded
A	Temperature	°C	20	40	−1	0	1
B	Adsorbent dose	g/l	0.5	2.5	−1	0	1
C	pH		2	6	−1	0	1
D	Initial metal ions concentration	ppm	20	100	−1	0	1

The biosorption data are used to evaluate various thermodynamics parameters, such as ΔH°, ΔG°, ΔE° and ΔS°.

2. Materials and methods

2.1. Source and genesis of fungal biomass adsorbent

The fungal strain *T. viride* was isolated from electroplating industrial soil. One gram of the soil was inoculated in the nutrient broth media amended with heavy metal ions solutions. The strain was isolated on nutrient agar media containing (g/l): agar 20.0, D-glucose 10.0, Bacteriological Peptone 5.0, KH_2PO_4 1.0, $MgSO_4{\cdot}7H_2O$ 0.5, Streptomycin 0.03, Agar 15.0 and pH 6.0 ± 0.5. The pure colony was preserved on the slants at 4 °C and identified from Microbial Type Culture Collection on the basis of spore's morphology. The fungal biomass was prepared in the nutrient broth by inoculating the spore suspension in the 250 ml flasks containing 100 ml of nutrient broth on the rotary shaker cum incubator at 35 °C and 125 rpm. The fully cultured biomass was harvested, filtered through sieve and washed with double distilled water. The biomass was dried at 50 °C and preserved in the polythene bags for the bisorption study.

2.2. Response surface methodology

Box–Behnken design of four variables and three levels each with three concentric point combination [9] was used to unearth the optimum pH, temperature, initial metal ions concentration and adsorbent dose. The design was taken as it fulfills most of the requirement for optimization of the biosorption study. The main objective of RSM is to determine the optimum operational conditions of the process that satisfies the operating specifications [10]. The Box–Behnken design of quadratic model contained 29 experiments for each metal ion.

2.3. Design variables of biosorption study

The design variables of Box–Behnken for bioremediation include: adsorbent loading (0.5–2.5 g/l), initial metal ions concentration (20–100 ppm), temperature (20–40 °C) and pH was selected (2–6) to avoid the interference due to precipitation at higher pH. The biosorption experiments were carried out at 120 rpm for 1 h of equilibrium period. pH of the synthetic solution was adjust using 1N NaOH/HCl. Three levels for each design variables for Box–Behnken for confined biosorption are listed in Table 1.

Various metals ions solutions were made using 1000 ppm stock solution prepared from $Pb(NO_3)$, $3CdSO_4{\cdot}8H_2O$ and $CuSO_4{\cdot}5H_2O$. The residual heavy metals ions quantification was analyzed by Atomic Absorption Spectrophotometer (Shimadzu AA-6300, Japan). The amount of heavy metal ions removal was obtained by using the following expression:

$$\%\,\text{Removal} = \frac{C_{initial} - C_{final}}{C_{initial}} \times 100 \quad (1)$$

where $C_{initial}$ is the metal ions concentration before equilibrium, C_{final} is the metals ions concentration after 1 h equilibrium period.

2.4. Design of experiments

Optimization is a research area with a long tradition, particularly in the field of operational analysis, which has given rise to a wealth of techniques. In conventional one-factor-at-a-time experimentation, effect of interaction among the factors is ignored as the experimenter varies a single factor, while other factors are held as constant. Response surface methodology is a systematic statistical approach to explore the relationships between design variables and responses that can give a better overall understanding with the minimal number of experiment runs. The Box–Behnken creates designs with desirable statistical properties but, most importantly, with only a fraction of the trials required for a 3-level factorial so the quadratic model is appropriate. The number of experiments required for Box–Behnken design can be calculated as follows:

$$N = k^2 + k + cp \quad (2)$$

where k is the factor number and cp is the replicate number of the central point [11]. Response surface methodology uses quantitative data in an experimental design to determine, and simultaneously solve multivariate equations, to optimize processes and products [12]. For the better accuracy, the second-order model is used. The general form for the second-order model is expressed as

$$Y = b0 + b1A + b2B + b3C + b12AB + b13AC + \cdots \quad (3)$$

where Y is the response, bn is the coefficient associated with factor n, and the letters, $A, B, C, \ldots$ represent the variables in the model.

2.5. Fourier transforms infrared (FTIR) spectroscopy

FTIR spectrum study was carried out to explain biosorption mechanism for identifying the presence of functionalities of the fungal biomass. The spectra were collected using PerkinElmer spectrum BX FTIR system (Beaconfield Buckinghamshire HP9 1QA) equipped with diffuse reflectance accessory with the range of 400–4000 cm^{-1}. To get the information specific to the group, and also on the interaction of the group with other parts of the molecule and on the spatial properties of the group by FTIR, the biosorption study for the metal ions were carried out holding temperature 30 °C, adsorbent loading 1.5 g/l and initial metal ions concentration 60 ppm at the central design point. pH the fourth most important parameter was adjusted according to the optimum point design by the model. The adsorption equilibrium experiments for FTIR study were carried out for 1 h at 120 rpm. The control pure biomass adsorbent was also run parallel in the distilled water at optimum pH. After equilibrium the metal loaded biomass was filtered through Watmaan filter paper and washed with double distilled water to remove the loosely bind ions or impurities. The metals loaded and pure biomass was dried at 50 °C in a heating oven. The samples were grounded in an agate pestle and mortar with KBr. The background obtained from KBr disc was automatically subtracted from the sample discs spectra prepared with KBr. All spectra were plotted using the same scale on the transmittance axis.