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# Evaluation of a newly developed biosorbent using packed bed column for possible application in the treatment of industrial effluents for removal of cadmium ions

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ABSTRACT

Removal of cadmium ions was investigated using a newly developed biosorbent namely immobilized *Bacillus subtilis* beads in continuous flow packed bed column. In the bench scale reactor three packed bed columns with variable diameter and bed depth, were used. The effect of flow rate and initial metal ion concentration was also investigated. The experimental data was analyzed and model parameters were evaluated. Highest uptake capacity of 104.2 mg/g was obtained for cadmium ion influent concentration of 30.04 mg/L, column bed depth of 50 cm, flow rate of 5 ml/min and column internal diameter of 2.4 cm. Cyclic use of the biosorbent was also investigated and results demonstrated its suitability for industrial use. The value of the determination coefficient of Artificial Neural Network (ANN) model for prediction of breakthrough curves was found to be 0.99. It exhibited excellent capability of ANN model for predicting breakthrough curves and model coefficients. The estimated cost of treatment, using new biosorbent, was found to be $ 1.92 per cubic meter of wastewater.



## 1. Introduction

Heavy metals pollution in water bodies is a great threat to the natural ecosystems and public health. These are toxic even at low concentrations and are major inorganic pollutants in the environment because of their mobility and toxicity. The cadmium is highly toxic and carcinogenic element [1]. It causes renal dysfunction (Fanconi syndrome), bone degeneration (itai–itai syndrome), disturbance in cardiovascular system, emphysema, cancer, kidney and liver damage [2]. Cadmium is present in industrial effluents of electroplating, batteries, paints, mineral processing, refining processes and alloy industry [3]. These industrial effluents require mandatory treatment for their safe disposal into natural ecosystems.

UK Department of Environment classified cadmium as priority pollutant in red list [4]. European Union has placed cadmium in black list of compounds and has directed to eliminate it on priority basis [5].

The conventional physico-chemical methods are either inadequate or very costly for the treatment of heavy metals, especially in low concentration range *i.e.* 1–100 mg/L. Secondly, the safe disposal of toxic sludge generated as a result of these processes is another issue [6]. These problems inspired the researchers to find alternate solutions which could offer such technique that is economically feasible and is also free of the associated problems mentioned above.

Biosorption has proven itself a cost effective, efficient and environmental friendly technology for sequestering the heavy metals from aqueous solutions. The biosorption phenomena has been extensively investigated and reported in literature [7–19]. However, in most of the previous laboratory studies, the biosorbents were applied in powdered form which made their post separation difficult. Thus the biosorbent has to be discarded after a single use. In addition, it also results in production of toxic sludge. Due to these difficulties, these biosorbents could not be used commercially.

In view of the above, there was a need to transform the biosorbents in such a form that could make their repeated use possible. In this way, these can be successfully applied in the industrial application as a low cost substitute to the conventional techniques. Recently batch studies were performed by immobilizing different microbial biomasses and converting them into beads. Immobilized *Bacillus subtilis* biosorbent (IBSB), Immobilized *Bacillus licheniformis* biosorbent (IBLB), Immobilized *Candida tropicalis* biosorbent (ICTB) and Immobilized *Candida utilis* biosorbent (ICUB) were examined. Among these, IBSB exhibited the best performance for the removal of cadmium ions. The results showed that

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**Nomenclature**

| Symbol | Definition |
|---|---|
| $a$ | constant for Yan's model |
| $A$ | area under the plot of $C_{ad}$ *versus* $t$ |
| $C_{ad}$ | adsorbed concentration of cadmium ions (mg/L) |
| $C_o$ | influent cadmium ions concentration (mg/L) |
| $C_{metal}$ | concentration of cadmium ion in regenerated effluent (mg/L) |
| $C_t$ | effluent cadmium ion concentration (mg/L) at time $t$ |
| $k_{AB}$ | Bohart–Adams rate constant (L/mg.h) |
| $k_{TH}$ | Thomas rate constant (L/mg.h) |
| $m$ | mass of the biosorbent in packed bed column (g) |
| $m_{total}$ | total cadmium ion fed into column (mg) |
| MTZ | length of mass transfer zone (cm) |
| $N_o$ | maximum volumetric biosorption capacity of bed (mg/L) |
| $Q$ | volumetric flow rate (ml/min) |
| $q_{exp}$ | experimental cadmium uptake capacity of packed bed column (mg/g) |
| $q_o$ | maximum solid phase concentration of the metal ions (mg/g) |
| $q_{total}$ | total adsorbed quantity of cadmium ions (mg) |
| $t$ | time (h) |
| $t_b$ | column breakthrough time (h) |
| $t_e$ | column exhaustion time (h) |
| $u$ | linear velocity which is flow rate per unit cross sectional area (cm/h) |
| $V$ | throughput volume (L) which is product of flow rate and time |
| $V_{HCl}$ | volume of 0.1 M HCl used as desorbing agent |
| $Z$ | packed column depth (cm) |

biosorption capacity of IBSB was 251.9 mg/g and it outclassed all other previously tested biosorbents [8].

IBSB performed better because it contained gram positive bacteria. These bacteria have greater capability to bind the metals due to their cell wall structure, in which carboxyl groups play an important role in the biosorption of heavy metal ions. In addition, the regeneration of heavy metal loaded IBSB was also investigated. It was ascertained that the regeneration of IBSB is possible using 0.1 M HCl. There was little loss in removal efficiency of IBSB after 5 cycles of biosorption and desorption. Regeneration also solved the problem of cyclic use of the IBSB and paved the way for exploring the possibility of its commercial application [8].

Most of the previous studies were restricted to batch biosorption process using the bacteria, algae, fungi and agricultural waste material. However, batch equilibrium biosorption data may not be applicable to continuous treatment system where residence time is lesser than equilibrium time. A packed bed column study is, therefore, required.

Breakthrough curves are used to evaluate the performance of packed bed column. These curves represent the ratio of effluent and influent concentrations of metal ions *versus* time profile. Modeling of breakthrough curves is carried out using the equilibrium, mass transfer and kinetics equations (numerical model). However the major issue with this method is extensive involvement of nonlinear mathematical equations and sometimes the required parameters could not be determined due to nonconvergence [20]. Alternately, empirical models may also be employed to determine breakthrough curves. Most commonly used are Bohart–Adams model, Thomas model and Yan model [20–23]. Nevertheless, these models bear the restriction of their use in explicit experimental conditions only hence making them unacceptable for varying experimental conditions. These may not be employed when the experimental conditions change.

Artificial Neural Network (ANN) is a powerful data modeling tool that has been successfully applied to model complex nonlinear relationships. It overcomes the aforementioned limitations of numerical and empirical models. Once ANN Model is applied and validated through experimental data, it may be used to predict the breakthrough curves and performance under a variety of operating conditions. This is the major benefit of using ANN [24–26].

In view of the above, the current study was conducted with the following objectives: (1) to investigate the removal of cadmium ions using IBSB in a continuous packed bed column for evaluation of its possible applications in industrial effluents treatment; (2) to analyze the column data using empirical models *viz.* models Bohart–Adams model, Thomas model, Yan model and (3) to study the possibility of using ANN to predict the removal of cadmium ions and breakthrough curves.

## 2. Materials and methods

### 2.1. Preparation of immobilized biosorbent

The fresh slants of pure cultures of *Bacillus subtilis* (NRRL NRS-1315) were collected from Institute of Industrial Biotechnology, Government College University (Lahore, Pakistan). The Biomass of *Bacillus subtilis* was grown using the Nutrient Broth (Oxoid, England) as culture media. IBSB was prepared using the calcium alginate gel and *Bacillus subtilis* biomass as detailed by Ahmad et al. [8].

### 2.2. Cadmium ions solution

A stock solution of cadmium ions was prepared by dissolving appropriate amount of analytical grade cadmium sulfate, $3CdSO_4{\cdot}8H_2O$, (Merck–Germany) in deionized water. All the working solutions of specific concentrations were prepared from the dilution of the stock solution.

### 2.3. Packed bed column studies

Packed bed column experiments were performed using three cylindrical glass columns (Fig. 1) with internal diameters of 1.5, 2.4 and 3.0 cm. At the top of the column, an adjustable porous plunger of teflon was used to change the effective depth of the column. The biosorption experiments were carried at the effective depth of 20 cm, 35 cm and 50 cm. A three-way valve was used to change the column between the biosorption and desorption cycle. The column packed with IBSB was operated in down flow mode using peristaltic pump for the biosorption and desorption studies. The effluent samples were collected at regular time interval and concentrations of cadmium ions in the influent and effluent were analyzed using atomic absorption spectrometer (Perkin Elmer – Singapore, AAnlyst 800).

The effect of flow rate was investigated at 5, 10 and 20 ml/min (5, 10 and 15 ml/min) for column bed depth of 50 cm and internal diameter of 2.4 cm. Similarly, the effect of influent concentration of 15, 30 and 60 mg/L was studied for column bed depth of 50 cm and internal diameter of 2.4 cm. The effect of internal diameter was studied using the three columns with internal diameter of 1.5, 2.4 and 3 cm for 20 ml/min flow rate, 50 cm bed depth and 30 mg/L initial concentration of cadmium ions.

All these experiments were performed at room temperature of $18 \pm 2$ °C. The initial pH of the cadmium ions solution was kept in a range of 5.18–5.92 which is the optimum pH value determined