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Hexavalent chromium biosorption studies using *Penicillium griseofulvum* MSR1 a novel isolate from tannery effluent site: Box–Behnken optimization, equilibrium, kinetics and thermodynamic studies

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ABSTRACT

This study reports the biosorption of Cr(VI) using a new indigenous fungal biosorbent *Penicillium griseofulvum* MSR1, which was isolated from locally sourced tannery effluent site. Response surface methodology based on Box–Behnken design (BBD) was used for optimizing the key variables *viz.* biosorbent dosage, initial Cr(VI) concentration and contact time. The results of BBD showed maximum biosorption of about 79.9% at 2 g/L biosorbent dosage, 67.8 mg/L initial Cr(VI) concentration and at contact time of 37.5 min. Langmuir isotherm model fitted better to the obtained equilibrium data with maximum adsorption capacity of about 75.1 mg/g and the pseudo-second order model best described the biosorption kinetics. Thermodynamic parameters revealed that the process was spontaneous, feasible and endothermic in nature. Desorption studies revealed that the MSR1 biosorbent can be regenerated using 0.1 M HNO_3 and reused for further biosorption studies. The result implies that MSR1 is a cheap and promising biosorbent for the removal of Cr(VI) from wastewater.

1. Introduction

Rapid industrialization has resulted in the release of heavy metal containing waste into the environment, which has caused grave damage to ecosystems and human health. Being non biodegradable, heavy metals accumulate in living tissues, leading to serious and irreversible physiological disorders [1]. Heavy metals are documented to be toxic even at low concentrations in the humans, biological organisms as well as on the ecological systems [2]. Among the different heavy metals, chromium is one of the most common and highly toxic pollutants released worldwide into natural waters at elevated concentrations from industrial effluents worldwide [3]. In nature, chromium exists in two oxidation states *viz.* trivalent chromium and hexavalent chromium. Long term exposure to trivalent chromium is known to cause allergic skin reactions and cancer. However, hexavalent chromium is very toxic than trivalent chromium [4] and has been classified as Group "A" carcinogen because of its mutagenic, tetratogenic and carcinogenic nature [5,6]. Cr(VI) is highly mobile and hence most prevalent in wastewaters released from the industrial processes such as leather tanning, metal finishing, electroplating, metallurgy, dye, battery manufacturing and wood preservation industries [6,7]. The maximum permissible limit of Cr(VI) in domestic water supplies is at 0.05 mg/L, while the total chromium is regulated below 2.0 mg/L [8]. Cr(VI) contamination has become a major concern globally due to its deleterious effects, even at low concentrations, on the humans, plants, animals and ecosystems. Due to its toxic effects, the removal of Cr(VI) from waters and wastewaters is vital for the protection of public health and the environment.

Traditional methods, for the treatment of chromium contaminated wastewaters include electrochemical method, reverse osmosis, chemical precipitation, membrane process, ion exchange, liquid extraction, electro coagulation, electro dialysis, evaporation and adsorption on activated carbon. Nevertheless, these technologies have significant disadvantages, including incomplete or low Cr(VI) removal, high operating costs and capital, high consumptions of reagent and energy, and generation of toxic secondary pollutants which are difficult to be disposed off [6]. Additionally, these processes have been found ineffective to remove Cr(VI) at very low concentration in the range of 10–100 mg/L [4]. In this endeavour, emphasis was given for biosorption where the property of inactive, live or dead biomasses are exploited for binding and concentrating metal of interest from dilute aqueous solutions [9]. Biosorption has emerged as an alternative and sustainable strategy for the remediation of chromium containing wastewaters as it is of low cost, effective, regenerative and eco-friendly [10,11].

Biosorption of Cr(VI) mainly depend on the surface functional groups of microbial communities [12] and due to the fact that Cr(VI)

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contamination persist, the search for efficient biosorbent still continues. A variety of microorganisms *viz.* bacteria, fungi, yeast and algae [3,6,13–15] have been isolated and screened for the cleanup of Cr(VI) from aqueous environments till date. Among the main strains, fungal biomass is known for a high percentage of cell wall material with outstanding metal binding properties [16]. The cell wall of fungi is mainly composed of chitin, glucan, mannan, proteins and polymers which possess carboxyl, phosphoryl, hydroxyl, amino and imidazole functional groups at the surface. Additionally, fungi are fast growing, has adaptability to natural environments, of low cost and also available as an industrial by-product [6].

Therefore, in the present study, a dead biomass of fungus *Penicillium griseofulvum* MSR1 was used as biosorbent for the removal of Cr(VI) from aqueous solution for the first time. The aim of the present investigation was to optimize the various process parameters for Cr(VI) biosorption using response surface methodology (RSM). A three variable Box–Behnken design was used for determining the optimal conditions of the process. Along with this a detailed study was conducted for assessing the biosorption equilibrium employing different isotherm models, sorption kinetics to find the controlling mechanism as well as thermodynamic studies for sorption of Cr(VI) by the fungal biomass MSR1. Additionally, the reusability of the MSR1 biosorbent was evaluated under consecutive biosorption–desorption cycles and also the interaction between biosorbent and Cr(VI) was examined by Fourier transform infrared (FT-IR) analysis. Thus, to the best of our knowledge, this is the first report which flaunts the Cr(VI) biosorption potential of MSR1 fungal biomass and based on the results, the biosorbent could be exploited for the remediation of Cr(VI) contaminated wastewater.

2. Materials and methods

2.1. Chemicals and reagents

Analytical grade potassium dichromate ($K_2Cr_2O_7$) was purchased from Sigma Aldrich, Bangalore, India. A stock solution of 1000 mg/L $K_2Cr_2O_7$ was prepared using double distilled water and was diluted to various desired concentrations as required. All the other chemicals used in the study were of analytical grade.

2.2. Sampling

Soil samples were collected from the rhizosphere of the tannery waste dump site at Ranipet, Tamil Nadu, India in screw capped sterilized bottles and maintained at 4 °C until isolation.

2.3. Isolation of chromium resistant fungi

For isolating Cr(VI) resistant fungi, 1 g of the soil sample was serially diluted and was plated onto potato dextrose agar (PDA) (pH 5.6) plates autoclaved at 121 °C and 15 lb for 15 min. For the growth of fungal colonies, the PDA agar mixed with chloramphenicol antibiotic was used. After incubating for 3–4 days at 27 °C, the growth of morphologically different fungal colonies was observed. The effect of Cr(VI) on the growth of fungal isolates was determined in PDA agar plate supplemented with 50 mg/L chromium. The plates were again incubated at 27 °C for 3–4 days. The obtained pure fungal colony was designated as MSR1 strain and stored in PD agar at 4 °C for further analysis. For molecular identification, the fungal genomic DNA was isolated using Insta Gene TM matrix genomic DNA isolation kit and the partial sequencing of 18S rRNAITS region was carried out commercially by Yaazh Xenomics Inc., Chennai, India using universal primers, ITS1 (5′-TCCGTAGGTGAACCTGCGG-3′) and ITS4 (5′-TCCTCCGCTTATTGATATGC-3′). The nucleotide sequence data were deposited in the GenBank sequence database. The BLASTn online tool was used to find out the related sequences with known taxonomic details in the NCBI website database (http://www.ncbi.nlm.nih.gov/BLAST) to identify the strain MSR1 accurately.

2.4. Preparation of metal solution

A Cr(VI) metal stock solution was prepared by dissolving $K_2Cr_2O_7 \cdot 7H_2O$ in double distilled water. The desired pH of the working solution was maintained by the addition of 0.1 M HCl or NaOH solution at the beginning of the experiment and was not controlled further. Analysis of Cr(VI) concentration was done by an atomic absorption spectrophotometer (AAS) (AA6300 Shimadzu, Tokyo).

2.5. Preparation of biosorbent

For biosorbent preparation, the MSR1 strain was cultivated in Yeast extract Peptone Glucose (YPG), containing (g/L): 3.0 yeast extract, 10.0 peptone and 20.0 (D-) glucose broth for 3 days at 27 °C. After incubation, the MSR1 fungus mat was harvested from the broth, washed with generous amounts of distilled water and was dried at 50 °C for 24 h, before powdered in a mortar and pestle. The dried biomass of MSR1 strain was sieved through a 150-mesh sieve and then stored in a desiccator for further use.

2.6. Batch biosorption experiments

The Cr(VI) biosorption studies were performed using dried fungal biomass MSR1 in Cr(VI) solution. For biosorption efficiency optimization, the experiments were conducted at different biomass dosage (1–3 g/L) and initial Cr(VI) concentration (25–125 mg/L), in continuously stirred (120 rpm) conical flasks containing 50 mL of working solution with contact time varying from 15–60 min at pH 2.0 and 27 °C. Preliminary experiments revealed maximum Cr(VI) biosorption at pH 2.0 and temperature of 27 °C, when pH was varied from 1.0 to 7.0 and temperature from the range of 27 to 42 °C. Samples were withdrawn at designated intervals, filtered prior to Cr(VI) analysis using AAS. All the experiments were repeated thrice to confirm the results. The percentage removal and uptake capacity of Cr(VI) by fungal strain MSR1 were calculated using the formula:

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

$$q_e = \frac{Co - C_f}{M} \times V \quad (2)$$

where C_0 is the initial Cr(VI) concentration (mg/L), C_f is the final Cr(VI) concentration (mg/L), M is the mass of the fungal biosorbent MSR1 (g) and V, the volume of working solution used (L).

2.7. Experimental design

For the present study, a three factor Box–Behnken factorial design was applied for optimizing the Cr(VI) biosorption efficiency of the fungal strain MSR1. RSM is a collection of statistical and mathematical techniques used for evaluating the relationship between the number of controlled experimental factors and measured responses with reference to the selected one or more criteria. Box–Behnken model (BBD) is one of the frequently used response surface methodology (RSM) design.

The present experimental design consists of a total 15 experiments using three independent factors such as biosorbent dosage (X_1), initial Cr(VI) concentration (X_2) and contact time (X_3) for obtaining maximum Cr(VI) removal percentage as a dependent response. The highest, lowest and central values of the independent variables