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Adsorption of chromium supported with various column modelling studies through the synergistic influence of *Aspergillus* and cellulose

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ABSTRACT

Convergence of biotechnology and chemistry offers greener alternatives in environmental remediation. Hexavalent chromium is genotoxic and carcinogenic. The aim of the present study is to investigate the removal of hexavalent chromium from aqueous solution in batch and fixed bed column experiments using dead biomass of isolated *Aspergillus* fungal species immobilized in epichlorohydrin crosslinked cellulose. The biosorbent exhibited good potential to remove Cr(VI). Other parameters such as pH, isotherms, kinetics and temperature effect were studied with a view to understand the adsorption efficiency. Biomass as low as 0.4 g could adsorb completely a Cr(VI) concentration of 5 mg L^{-1} within 3 h from an aqueous volume of 30 mL. Optimum pH and temperature for Cr(VI) biosorption were 2.0 and 30 °C, respectively with a Langmuir adsorption capacity of 23.83 mg g^{-1}. Kinetic studies favour the pseudo second order model. The biosorbent–Cr(VI) interactions were corroborated by FTIR, SEM, EDAX and ESCA analysis. Emphasis is laid on various column modelling studies at different bed heights, flowrates, and concentrations of Cr(VI) and the experimental data obtained was in good agreement with Bed Depth Service Time (BDST) model. The synergism of *Aspergillus* and cellulose as a potential biosorbent was also validated in a synthetic mixture of diverse ions and a certified industrial effluent wastewater sample (BCR-715).

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1. Introduction

The presence of heavy metals such as Cd, Cr, Hg, Cu, Pb, Ni, Zn etc., beyond the tolerance limit is a serious environmental concern [1,2]. Chromium has extensive industrial applications and the waste water from mining, electroplating, dyes and leather tanneries etc [3] are some of the probable sources for chromium contamination. Chromium exists in various oxidation states, but the trivalent and hexavalent forms are predominant and they contaminate the ground water through the wastewater discharge from chrome based industries. Major source of Cr(VI) contamination is from electroplating industries while leather tanneries release considerable amounts of Cr(III). Cr(III) in trace amounts functions as a nutrient for lipid and glucose metabolism [4,5]. The manganese oxides in the soil can oxidize it to the more harmful +6 state. Hexavalent chromium, being an oxy anion ($HCrO_4^-$, $Cr_2O_7^{2-}$, CrO_4^{2-}) has higher solubility and mobility in aqueous medium than the cationic Cr(III) [6]. Intracellularly, hydrogen peroxide, ascorbic acid and glutathione reductase can augment the reduction of Cr(VI) to yield reactive intermediates and disrupt the functioning of DNA, proteins and lipids. The chronic exposure to Cr(VI) could also lead to renal, respiratory, gastrointestinal, cardiovascular and haematological ailments [7,8]. The United States Environmental Protection Agency [9] recommends the chromium level in water as less than 0.1 mg L^{-1}. Hence it is important to develop as well as improvise upon the existing techniques for chromium removal from the effluents prior to the discharge into the environment.

Conventional strategies such as coagulation, precipitation, ion exchange, membrane separation that are viable for removal of pollutants from water are associated with increased sludge formation, higher capital cost, fouling of resins etc [10,11]. Fundamental studies have proved that adsorption is a promising method in diverse industrial applications because of low cost, easy mode of operation and abundant availability of various adsorptive materials [12]. Adsorbents such as activated carbon [13], raw and modified lignocellulosic materials [14], iron oxide [15], graphene oxide [16] etc. are quite useful for Cr(VI) removal. Greener

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alternatives such as biosorbents which involve the use of microbes and biopolymers are more environmentally benign in nature. The functional groups inherently available on the surface of bacteria, fungi or algae aid in metal complexation and ion exchange during the heavy metal remediation [17]. However direct applications of biomass for large scale applications has some drawbacks in terms of leaching of microbes, low regeneration capacity and loss of biomass. Hence it is important to consider the immobilisation of microbes in various supporting matrices to attain good mechanical strength and porosity thereby enhancing the metal removal efficiency [18,19]. Dead microbes are endowed with higher surface area, easy storage and handling compared to live microbial cells in which there is a requirement for uninterrupted nutrient supply. Detoxification of metals by non-living biomass is a metabolism independent process and referred commonly as a passive biosorption mechanism [20]. Some of the recently reported biosorbents for chromium(VI) reduction and removal include 97% reduction of Cr(VI) to Cr(III) from a chrome(VI) tannery effluent by *Trichoderma* fungal species [21]. It has been reported by Park et al. [22] that with biomass involving chromium adsorption, there is a probability of adsorption coupled reduction mechanism. Since, biomass is also a rich source of carbon, the reduction is possible through the adsorption of cationic Cr(III) on the biosorbent surface.

A modified fungal biomass of *Penicillium chrysogenum* by grafting polyethylenimine on its surface [23] shows good efficacy in the adsorption of chromium(VI). The mechanism involves the adsorption as well as partial reduction of +6 to +3 state and were confirmed through XPS studies. Sujoy et al. [24] reported the interaction of chromium with *Aspergillus versicolor* using Atomic force microscopy (AFM) and Transmission electron microscopies (TEM) and the XPS, FTIR studies revealed that bound Cr was in the form Cr(III) involving adsorption coupled reduction. Mungasavalli et al. [25] reported that the pre-treated *Aspergillus niger* could adsorb chromium effectively with 15.2 mg g^{-1} Langmuir adsorption capacity, *Aspergillus sp* immobilized in sodium montmorillonite is reported to have good potential for Cr(VI) removal with an adsorption capacity of 45.67 mg g^{-1} [26]. Microwave assisted preparation of biosorbent such as yeast immobilized in cellulose can efficiently remove Cr(VI) with an adsorption capacity of 23.61 mg g^{-1} [27]. The lipase enzymes secreted by the fungal species such as *Aspergillus* finds applications as biocatalyst in various industrial processes such as additives to detergents, synthesis of enantiopure drugs and food ingredients [28,29]. The xylanase enzyme produced by *Aspergillus* is also used for biobleaching [30].

Biopolymers such as cellulose and chitosan function as good supports for chromium removal as they are easily available at low cost and are also degradable [31,32]. The numerous methods available for removal of chromium using batch studies have some limitations during scale up operations. There are few reports on the successful pilot scale up studies for the removal of Cr(VI) using a biofilm of *Arthrobacter viscosus* supported on granular activated carbon [33] and also by reduction with ferrous sulfate [34]. Fixed bed column studies are operative in the treatment of larger volumes of the heavy metals contaminated waste water [35]. The column modelling studies aid in understanding the various characteristics as well as limitations in the design of larger columns in industrial treatment operations. The present study explores the utility of the *Aspergillus* immobilized in epichlorohydrin crosslinked cellulose biosorbent for chromium removal. Batch studies are done prior to column adsorption in order to understand the efficacy at a small scale. Although, the aim of the study is column adsorption, preliminary batch studies were undertaken to optimize the pH, variation in the amount of adsorbent, isotherms, time required for maximum adsorption of Cr(VI) and the temperature at which adsorption is effective along with spontaneity (through free energy and entropy changes) and heat of adsorption (through enthalpy changes). The batch experimental studies aid in understanding several features about the adsorbent-adsorbate interaction and the maximum adsorption capacity that would be useful in column design along with optimizing the other vital column parameters such as bed height, flow rate etc. Subsequently, column modelling studies were investigated at room temperature correlating the above factors.

2. Experimental procedure

2.1. Materials and methods

The filamentous fungi was isolated from bread mould and the strain (*Aspergillus* BRVR) was confirmed through DNA isolation, Polymerase Chain Reaction and sequencing with a Gen bank accession number KT699195 as reported by our group previously [26]. The fungi was maintained on a Sabaroud Dextrose medium and the biomass was dried overnight at 70 °C [36], ground to a fine powder and used in the biosorption studies.

Analytical and guaranteed reagents were used in the experiments. The matrix used was cellulose which was procured from Himedia (India), the cross linking agent epichlorohydrin from Sisco Research laboratories, India and sodium hydroxide was obtained from Merck. The aqueous solutions of $K_2Cr_2O_7$ (G.R, Merck) were prepared in Millipore water. A simple stock solution of 1.0 g L^{-1} of $K_2Cr_2O_7$ and different working solutions were prepared accordingly to optimize the batch and column experiments. The certified industrial effluent wastewater sample (BCR-715) was procured from IRRM-European Commission Joint Research Centre, Belgium.

4 g of cellulose was taken in a 100 mL beaker and 25 mL of 2.0 mol L^{-1} sodium hydroxide, 4 mL of epichlorohydrin (as cross linker) were added and stirred for 120 min at 55 °C [37]. An equal amount of the powdered fungal strain was added and stirred further for 60 min. The obtained biosorbent was washed with Millipore water and dried overnight at 40 °C in a vacuum oven.

2.2. Characterisation

The prepared *Aspergillus*-cellulose biosorbent was characterised using various techniques. A JASCO – 4200 FTIR was used to record the FTIR spectrum and pellatization was done by mixing 100 mg KBr with 1 mg of biosorbent in the range 4000 cm^{-1}-400 cm^{-1} at 4 cm^{-1} resolution. Cr(VI) was estimated using a post column derivative method in 883 Basic IC plus ion chromatography (Metrohm,887 UV visible detector, Switzerland) and also spectrophotometrically using a Jasco V650 model UV–vis spectrophotometer. SEM images of the biosorbent was taken using a S3400 N Scanning electron microscope (Hitachi) associated with an EDAX analysis system (Thermo Electron Corporation). Shimadzu (DTG-60) thermal analyser was used for Thermal analysis (TGA) wherein the samples were heated in the range 30 °C–800 °C at the rate of 10 °C min^{-1} under nitrogen atmosphere. The surface area and pore size of the biosorbent were analysed using a Smart Sorb 92/93 model surface area analyser (Smart Instruments Company Private Limited, India). The high resolution XPS (Omicron, Nanotech) spectra were recorded using an X-ray power of 300 W, 15 KV using Mg Kα source of 1.253 keV. The solution pH was monitored using an Elico LI 127 (Elico, India) pH meter equipped with combined glass-calomel electrode.

2.3. Batch adsorption studies

A 0.4 g amount of the *Aspergillus*-cellulose biosorbent was mixed with 30 mL of Cr(VI) of various working solution

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