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Removal of CR (III) from model solutions by isolated *Aspergillus niger* and *Aspergillus oryzae* living microorganisms: Equilibrium and kinetic studies

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ABSTRACT

Biosorption by fungi is a efficient method for removal of heavy metals which have been recently used by many researchers. The aim of the present work was the seeking and the isolation of sustainable microorganisms and their application for the removal of Cr (III) from simulated and real solutions. To isolate sustainable microorganisms, soil samples were taken from rawhide, tannery tanks and effluents discharged environment. *Aspergillus niger* and *Aspergillus oryzae* were the two types of isolated fungi from tanning factory environment. Fungal growth and chromium removal efficiency were studied as a function of maximum fungal tolerance to Cr (III) concentration, pH, temperature, contact time, agitation speed and nutrients addition. The optimal conditions for fungal growth were 30 h at pH 5.2, an agitation speed of 150 rpm and 30 °C in a medium containing yeast powder and di-hydrogen ammonium phosphate as nutrients. Maximum biomass concentration increased from 0.8 to 4 g/L for both fungi in the above mentioned conditions. Maximum fungal tolerance and chromium removal were found to be 600 mg/L and 95–98% of Cr (III). Equilibrium data were found to follow a Langmuir isotherm model and maximum sorption capacities were 185 and 208 mg/g for *A. niger* and *A. oryzae*, respectively. Experimental data was accurately fitted onto pseudo-second order kinetic model. Promissing results were also recorded on a real effluent, since in the above optimal conditions, chromium removal yields were 72 and 67% for *A. niger* and *A. oryzae*, respectively. However and owing to the high variability of the effluent, subsequent work is needed to confirm these positive results irrespective of the characteristics of the inlet effluent.

1. Introduction

Wastewater containing heavy metals are serious contamination source of surface and ground water resource all over the world [1]. Heavy metals such as chromium, lead and mercury can accumulate in living organism tissues and then introduced into the human food chain. Chromium is one of the heavy metals usually introduced into the environment through industrial effluents such as metal plating, wood processing, leather tanning, paint and pigments, steel fabrication and other activities [2]. In the environment, chromium mainly exits in the form of Cr (VI) and Cr (III). Hexavalent chromium is significantly more toxic than trivalent chromium due to its high solubility and significant mobility in the environment [3,4]. However, in tanning effluents trivalent chromium is preponderant and also shows toxicity, as shown for fish for concentrations in water exceeding 5 mg/L. Its oxidation to the more carcinogenic and mutagenic Cr (VI) by MnO_2 in the environment or by some bacteria has been also reported. In addition, it is classified in group 3 (with lower evidence for generation of cancer in human) by the International Institute for Cancer Research [5]. Recently, several methods such as zeolitic materials [6], polyaniline–Polyethylene glycol composite [7], *Spirulina platensis* biomass [8], anaerobic process [9], and bimetallic particles [10] have been used for the removal of chromium from real or synthetic solutions. In addition, recently many researchers used living and non-living microorganism for the removal of various pollutants such as Zn^{2+} [11], chromium [12] and dyes [13]. The removal of contaminants by adapted and isolated microorganisms is an attractive method due to its feasibility, economical feature and the absence of by-products. Among the available microorganisms, fungi have been implemented for the removal of non-biodegradable pollutants such as heavy metals [14]. Wastewater from Tanning industry usually contains high level of both Cr (VI) and Cr (III). In addition, such effluents show acidic pH and nutrients deficiency. Since Cr (III) is the major species in tanning effluents, the implementation of microorganisms isolated in the environment of tanning industry located in the

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south region of Tehran for the removal of Cr (III) from model and real solutions was the purpose of this work. To the best of our knowledge, its removal by living microorganisms was not previously investigated. In addition, owing to the differences between the implementation of living microorganisms and dead cells which are usually considered, investigation of optimal growth conditions may be helpful for extrapolation to real effluents at large scale and to other toxic heavy metals.

2. Materials and methods

2.1. Sampling and isolation of probable microorganism

Samples from rawhide and tannery tanks, as well as samples from effluents discharged environment, were taken. The samples were cultured for seeking possible relevant microorganisms. Antibiotics were added to inhibit bacterial growth; molasses was used as growth culture. Since the aim of this work was to identify and isolate fungal biomass, medium pH was adjusted to 5.5 by 1 N NaOH or H_2SO_4 additions. Plates were incubated at 30 °C upon 6 days. Microorganism culture revealed that various fungi are living in the environment of maintained tanning industry. Among these microorganisms, *Aspergillus niger* and *Aspergillus oryzae* were selected. For identification purpose, the considered fungi were compared to the type species from the culture collection of the Organization of Scientific and Industrial Research of Iran. The isolated fungal strains was separated and kept in stock cultures at 4 °C.

2.2. Production and preparation of biosorbent

Potato dextrose agar containing 300 g potato, 20 g glucose, 15 g agar and 1 L distilled water was used for fungal culture. Fungal reactivation was done by adding a given volume (1 ml) of isolated fungi from a previous step (Section 2.1) to the appropriate culture medium. The culture was incubated at 30 °C for 6–7 days, and was then taken and used for experiments. To determine fungal biomass, a given amount of culture was filtered. After that, the filter was dried at 103 °C for 6 h and then weighed again. The fungal mass was determined by subtracting the filter weight after and before filtration.

2.3. Chemicals and instruments

All chemicals used in this work were of GR grade and obtained from Merck. 1 N NaOH and H_2SO_4 were used to adjust pH (model Sartorius Professional Meter PP-50). Since the main chromium ions in tanning industry is Cr (III), stock solution was prepared by adding appropriate amount of $Cr(NO_3)_3$ onto de-ionized water. The chromium concentration was determined by atomic absorption spectrometer (Model Alpha4-Chemtech, England).

2.4. Batch experiments

Experiments were conducted in 250 ml beakers. All experiments were done according to standard methods for the examination of water and wastewater [15]. Various parameters such as pH (3–8), contact time (0.5–38 h), agitation speed (50–250 rpm), nutrients addition (di-hydrogen ammonium phosphate and yeast powder) and solution temperature (10–45 °C) were investigated. To perform experiments, a specified amount of living fungi was (initially 0.8 g/L) added to 100 ml chromium solution at various pH. The broth was stirred at 150 rpm, maintained at 30 °C for 38 h until reaching equilibrium. Then and after sample filtration, final chromium concentration was measured by atomic absorption spectrometer. The removal efficiency was calculated using the following equation:

$$q_e = \frac{(C_0 - C_e) \times V}{M} \quad (1)$$

where q_e (mg/g) is the equilibrium concentration of chromium, C_0 and C_e (mg/L) are the initial and final concentration of Cr (III), respectively; V (liter) is the volume of solution and M (gram) is the mass of biosorbent.

3. Results and discussion

3.1. Effect of the contact time

It was investigated in the range of 0.5–38 h. The results are shown in Fig. 1. For increasing contact time, fungal biomass increased until reaching stationary state after 30 h culture. The initial fungal mass was 0.8 g/L and reached 3.3 and 2.8 g/L for *A. niger* and *A. oryzae*, respectively. Chromium removal was clearly linked to growth, since it increased during culture until reaching a stationary level at stationary growth phase, after about 30 h. Biosorption using living microorganisms showed therefore a different trend to that usually observed in adsorption process, namely a fast initial uptake rate [1,16]. Following growth behavior, Cr (III) sorption rate was initially low and increased until reaching equilibrium after 30 h contact time. Removal efficiencies were 27 and 32% after 0.5 h and increased to 97% after 30 h of culture for

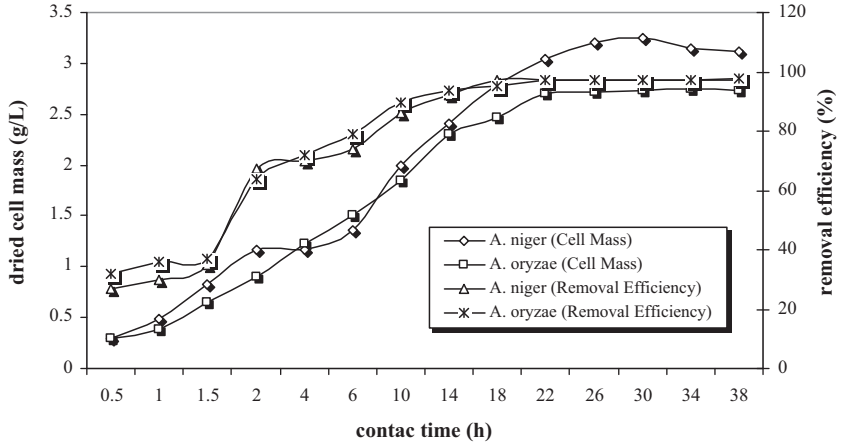

Fig. 1. Effect of the contact time on fungal growth and removal efficiency during *A. niger* and *A. oryzae* growth in presence of 240 mg/L initial chromium concentration, at pH 5.5, 30 °C and 150 rpm agitation speed.