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Biosorption of Lead and Chromium Ions by Using *Penicillium digitatum* (Pers.) Sacc. from Industrial Water

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Abstract

Some microorganisms, including fungi, are characterized by their removal efficiency and reducing the concentrations of heavy metals such as Pb and Cr from industrial water. The present study aims to estimate the efficiency of *Penicillium digitatum* (Pers.) Sacc. as a low-cost biosorbent in reducing Pb and Cr from industrial water with optimum biosorption conditions (acidity of 1.5 , 4, and 5; temperature of 30 °C). The Fourier transform infrared spectroscopy (FTIR) analysis was also used for determining the roles of the functional groups in this biosorbent. The results indicated that the highest *P. digitatum* efficiency values for reducing the levels of Pb and Cr were 84% and 70% , respectively, at pH of 5 after 24 h. However, this efficiency was decreased from 81% to76% at pH values of 4 and 1.5, respectively, for Pb. The removal efficiency for Cr was 56% at pH of 4 after 1h. at 30 °C. Also, the FTIR spectra illustrated -CH, -C-N, N-H, and =CO peaks of functional groups that may change as a result of their involvement in the adsorption process of lead and chromium.

Keywords: Heavy metals, *Penicillium digitatum*, removal efficiency and biosorption

الامتزاز الحيوي لعنصري الرصاص والكروم من مياه الصرف الصناعي باستخدام فطر *Penicillium digitatum* (Pers.) Sacc

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الخلاصة

تمتاز بعض الاحياء المجهرية ومن ضمنها الفطريات بقابليتها على الامتزاز الحيوي وخفض تركيز المعادن الثقيلة من مياه الصرف الصناعي. اختبرت قابلية فطر *Penicillium digitatum* (Pers.) Sacc بوزن 0.1غم في عملية الامتزاز الحيوي لعنصري الرصاص والكروم تحت ظروف مسيطر عليها من مدى الدالة الحامضية 1.5و4 و5 ودرجة الحرارة 30ºم. تم استخدام جهاز تحويل فورييه الطيفي للأشعة تحت الحمراء (FTIR) لتحليل وتحديد المجاميع الفعالة للمادة الممتزة. اظهرت النتائج اعلى نسبة ازالة للفطر *P.digitatum* لعنصري الرصاص و الكروم 84% و70% عند دالة حامضية 5 وزمن تماس 24 ساعة على التوالي. بينما انخفضت كفاءة الازالة لعنصر الرصاص 81%الى76% في دوال حامضية 4 و 1.5 على التوالي. وكانت كفاءة الازالة لعنصر الكروم 56% عند دالة حامضية 4 خلال زمن تماس 1 ساعة.

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اظهر جهاز تحويل فورييه ان مواقع قمم المجاميع الفعالة قد تغير نتيجة اشتراكها في عملية امتزاز عنصري الرصاص والكروم.

1. Introduction

Water pollution is a worldwide issue that affects water ecosystems in daily life and caused by different industries that need huge quantities of water [1]. Agricultural, industrial and domestic wastewater is one of the main sources of pollution of the aquatic environment that is resulted from many organic and inorganic pollutants and heavy metals when discharged to surface water without proper treatment. These pollutants change the characteristics of natural water, where heavy elements are dangerous pollutants because of their toxic effects on the environment [2]. Industries that use heavy metals and their applications are problematic to the contemporary environment. Heavy metals discharge into the aquatic environment undoubtedly causes an imbalance of the ecosystem or poisoning aquatic plants, fish and other organisms in that environment. These elements are highly toxic to humans when they enter the food chain [3]. In a local study of heavy metals concentration in the water samples of tanning plants in AL-Nahrawan in Baghdad/Iraq, the authors found the highest concentration of Pb in discharged water from tanning plants which represents the external discharge channel was (3 ppm). Also, they noted that the concentration of Pb in most samples of discharged and untreated water exceeded the Iraqi standard (0.1 ppm) [4]. Methods for the removal of metal ions from aqueous solutions mainly include physical, chemical and biological techniques. Conventional methods for metals removal include chemical precipitation, filtration, ion exchange, electro dialysis, reverse osmosis (RO) and membrane separations [5]. All of these techniques are costly and not effective enough for treating large quantities of solutions, especially water, and are not used well in industrial water treatment with low concentrations of heavy metals [6]. Using biological treatment is an effective way for reducing heavy metal concentrations because it is environmental friendly, economical, simple to instrument, and do not require the skill. The biosorption process by fungi as an alternative treatment of wastewater containing heavy metal has a great importance at the present time to reduce these metals. The filamentous fungi play an effective role in reducing and removing many heavy elements in the soil and the aquatic environment [3]. Fungi have the ability to bind heavy metal ions; the initial mechanism for metal binding by microorganisms is electrostatic attraction between charged metal ions in solution and charged functional groups on microbial cell walls [7]. For removal of heavy metals from solutions, fungi were demonstrated as a potential biomass that belongs to the genera *Penicillium* and *Rhizopus* [8]. On the other hand, another study [9] reported promising biosorption for Cd and Cr by two filamentous fungi, *Aspergillus* sp. and *Rhizopus* sp. The aim of current study is the removal of toxic trace metals using biosorbant fungi.

2. Materials and methods

2.1 Sample Collection

Samples were collected from the State Battery Manufacturing Company / AL-Waziriya in Baghdad/Iraq in sterile glass bottles (1L). These samples were taken from a depth of 10-15cm from the treatment station. The concentrations of Pb and Cr before treatment were 2.7ppm and 0.3ppm, respectively. The metals' concentration analysis was accomplished in the Water Research Center/ Directorate of Water and Environment/ Ministry of Science and Technology. The experiment was carried out at optimum conditions to investigate the biosorbent efficiency of heavy metals removal from the industrial water.

2.2 Preparation of biosorbents

2.2.1 Non-living dried fungal biomass (adsorbent surface)

The isolated *Penicillium digitatum* was grown in potato dextrose broth at pH 5 and incubated at 28°C for 4-5 days, the biomass of *P. digitatum* fungi was harvested by filtration through filter papers No.1, rinsed several times with distilled water, and autoclaved for 15min at 121°C. Then, the biomass was dried in an oven at 50ºC for 24 hours. After that, the dried fungi biomass was powdered, sieved to 1.18 mm by a sieve (No. 16), and stored at room temperature for the determination of the dried biomass of biosorption fungi [10,11]. Metal concentrations in the industrial water were measured by atomic absorption spectrophotometer.

2.3 Factors affecting heavy metal biosorption from the aqueous solutions

The main examined parameters that may impact metal sorption were pH, contact time at 0.1g biosorbent, weight of *P. digitatum*, and temperature (30 °C) [12,13, 14].

2.2.3.1 Effects of pH value

The effects of pH parameter on Pb and Cr biosorption by fungi biomass were examined. The experiment was carried out (the pH values of industrial wastewater was 1.5 then change to 4 and 5) by using 0.1 M NaOH or HCL solution at 100 rpm agitation speed for periods of 0.5, 1.0, 1.5, 2.0 and 24 hr. at 30°C.

2.2.3.2Effects of contact time

The contact time effect on heavy metals removal by absorption was determined at different contact times of 0.5, 1.0, 1.5, 2.0 and 24 hr. at different pH values and a temperature of 30 °C in the industrial water taken from the treatment station. It was clear that the establishment of time dependence on the metal removal for maximizing the rate of these metals by biosorbent uptake during equilibrium. The time at which no further metals removal could be attained was considered as the optimum contact time [13].

2.4 Calculations

The following equations were used to calculate the efficiency of biosorption (η) by the difference between the initial and equilibrium concentrations of metal ions, according to the following equation [15]:

$$\eta = \frac{(C_o - C_e)}{C_o} \times 100$$

where:

η= The biosorption efficiency.

C_o = the initial metal concentration (mg/L).

C_e= the final concentration (mg/L).

3.Results and discussion

The following parameters affecting the biosorption efficiency of heavy metals removal from the aqueous solutions by *P. digitatum* were investigated.

3.1 pH values and contact time

The results of Pb and Cr removal efficiency by *P. digitatum*as biosorbent that were achieved under values of pH 1.5 , 4 and 5 and four different contact times (0.5, 1, 1.5, 2 and 24 hr.) are shown in (Figures- 1, 2 and 3). Figure-1 shows that the higher removal efficiency values for Pb by *P.digitatum* were 84 % and 40 % at pH 5 and 0.5, respectively, after 24hrs. While, the highest removal efficiency for Cr at pH 5 was 70% after 24hr. The removal efficiency of Pb was decreased from 81% at pH 4 and reached to 76% at pH 1.5 after 24hr (Figures- 2 and 3). On the other hand, the removal efficiency of Cr reached to 56% at pH 4 and decrease to 33% at pH 1.5 after 60min., as shown in Figures- 2 and 3.The results of this study were are inconsistent with those of an earlier report [16] that found the Pb ion uptake by *A. niger* ranged from 6.71 to 64.95% for dead biomass at optimized pH of 2, 4, 6 and 7. Metals uptake was occurring initially at pH 1.5 before rising to a maximum value at pH 5, which also showed the highest biosorption. The current results provide support to those of a previous work [17] which reported that Pb and Cr biosorption by *A. flavus* or *A. niger* biomass was higher at pH ranging from 4 to 5. The results of this study also agree with those reported by other authors [18] who found that the maximum biosorption of Cu and Zn ions (48.5 and 0.7%) is obtained at pH 4 and revealed that the removal efficiency of fungal groups decreases with the increase in pH. The optimal biosorption of Zn and Cu by *Saccharomyces cerevisiae* was reported to be achieved between pH 4 and 5. The biosorption of metals was decreased at a very low acidic pH of 1.5. On the other hand, another study [19] demonstrated that the proton concentration is higher at lower pH (<2) and that heavy metal biosorption decreases due to the positive charge density on metal binding sites, i.e. hydrogen ions compete effectively with metal ions in binding to these sites. The negative charge density on the cell surface increases with increasing pH due to the deprotonation of the metal binding sites. The metal ions then compete more effectively for available binding sites, which increases biosorption. The current study disagrees with an earlier investigation [20] which showed a maximum Pb removal efficiency by culture fungi after 2 hours. The results showed that the absorbent removal of metal ions was higher from the beginning until 24 hours and, therefore, the biosorption became very slow. These results can conclude that the contact time of 24 hours is sufficient to reach equilibrium or optimal conditions for binary heavy metals. Another study [21] found that the contact time for Pb removal rate was initiated in 30 min.by dead biomass in batch culture from synthetic metal solution and reached a maximum of 84% at 24 hrs. of biosorption treatment. Also, one of the important factors that may impact biosorption is the charge of microbial surfaces; the negative charge on the microbial surfaces may be due to the functional groups ionization by contributing to metal binding. It is clear that all the factors, including pH values, contact time, charge of biomass, and others can affect the biosorption process.

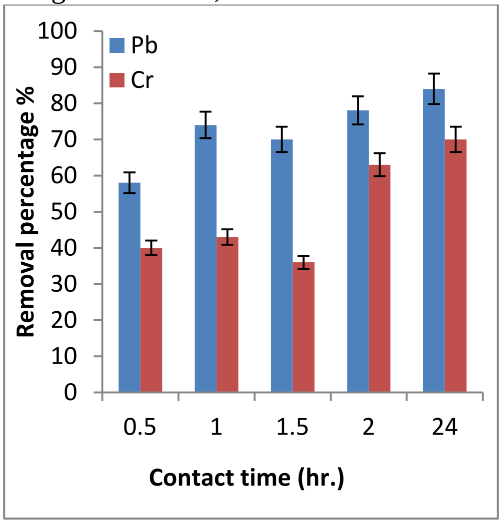

Figure 1-The removal efficiency (%) of Pb and Cr in binary mixtures by *P. digitatum* at pH 5.

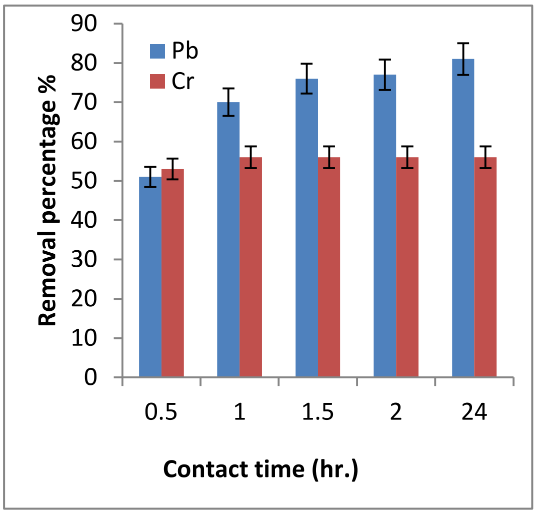

Figure 2-The removal efficiency (%) for Pb and Cr in binary mixtures by *P. digitatum* at pH 4.

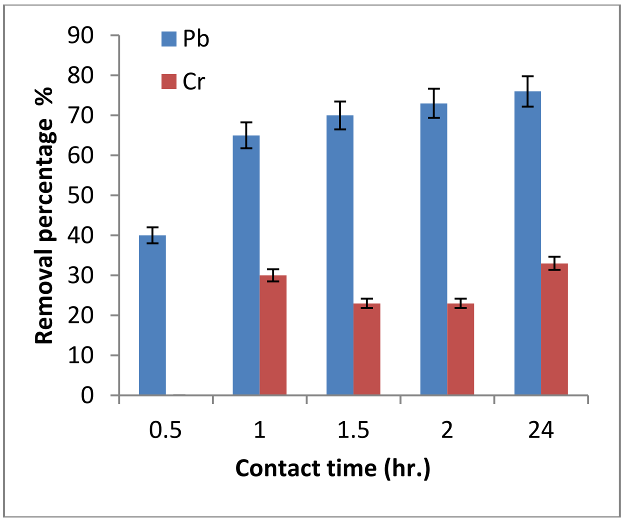

Figure 3-The removal efficiency (%) of Pb and Cr in binary mixtures by *P. digitatum* at pH 1.5.

3.2 Fourier transform infrared spectroscopy FTIR)

The FTIR spectrum was used to characterize the functional groups of *P. digitatum* fungi before and after biosorption process to obtain better binding to the surface of functional groups of different investigated biosorbents, which depends on the capability of fungal biosorption to Pb and Cr and the changing of functional groups absorbance. The chemical functional groups that appeared were the alkanes, hydroxyl, carboxyl, and an amine group. The figures confirmed that *P. digitatum* functional groups are responsible for metal binding before and after biosorption process. Figure- 4 and Table-1 show the possible metal binding sites in *P. digitatum* (Before and after biosorption), while Figure- 5 show the FTIR analysis of *P. digitatum* loaded with Pb and Cr .

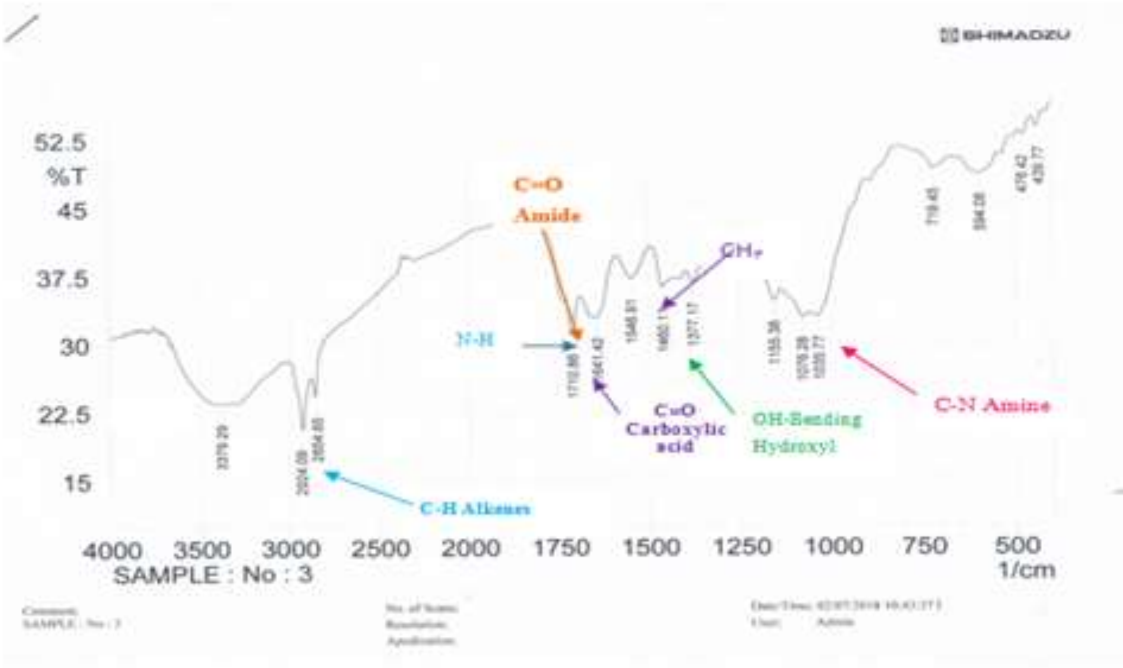

Figure 4-FTIR analysis of *P. digitatum* loaded with metals.

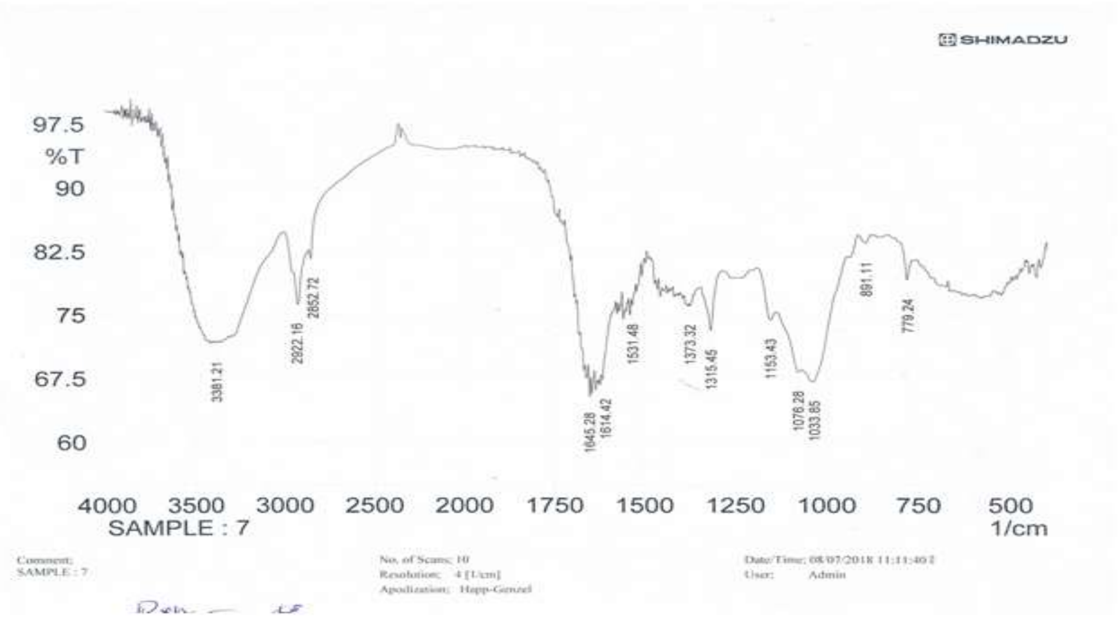

Figure 5-FTIR analysis of *P. digitatum* loaded with lead and chromium.

Table 1-The possible metal binding sites in *P.digitatum* (Before and after biosorption)

Values of Pb and Cr peaks before adsorption	Values of Pb and Cr peaks after adsorption	Functional group
2922.16	2924.09	CH (Alkanes)
1641.42	1614.42	C=O(Carboxylic Acid),NH- (Amine)
1460.11, 1377.17	1373.32, 1315.45	CH_3 (Bend)
1035.77	1033.85	C-N (Amine)

4. Conclusions

The examined biosorbent *P. digitatum* fungi are active in the removal of lead and chromium. The optimum condition for Pb and Cr biosorption was pH 5 for 24 hr. For binary component systems, Pb ions were the most favorable and the strongest component that were able to displace chromium ions. This was due to their competitive effects and physiochemical characteristics of less solubility and high molecular weight, which make it able to occupy the available sites of the *P. digitatum* biomass. The FTIR results illustrated that the functional groups, such as -CH, -C-N, N-H, and =CO, were found in all biosorbents and had important roles in Pb and Cr biosorption process.

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