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Biosorption of cadmium, manganese, nickel, lead, and zinc ions by *Aspergillus tamarii*

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ABSTRACT

In this paper, Cd^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} heavy metals ions adsorption properties of commercially obtained *Aspergillus tamarii* were investigated. The dead biomass was used with a batch system for experiments. The effect of the operating parameters, such as pH, temperature, agitation speed, contact time, initial metal concentration, and biomass dosage of aqueous solution containing Cd^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} was studied to find biosorption capacity. The optimum pH range for all heavy metal uptakes was 6.0. The experiments were carried out at different temperatures in the range of 20–50°C and the maximum uptake was found to be at 25°C. Heavy metal ion uptake increased with agitation speed until 150 rpm. After this agitation speed adsorption capacity slightly decreased. The adsorption equilibrium was obtained at 150 min contact time. At the optimal conditions, maximum uptake of Cd^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} was found to be 51.69, 46.99, 58.74, 98.14, and 54.33%, respectively, by using 1.5 g biomass. The interaction between heavy metals and biomass was characterized by FTIR spectroscopy.

Keywords: Aspergillus tamarii; Biosorption; Heavy metal; FTIR

1. Introduction

Heavy metal pollution is one of the major problems for environmental aspect. Most drinking water sources are contaminated with heavy metal ions by human activities. The World Health Organization has recommended the maximum acceptable concentration of Cd^{2+}, Ni^{2+}, and Pb^{2+} in drinking water as 0.003, 0.07, and 0.01 mg/L respectively [1]. Ion exchange [2], activated carbon adsorption [3], reverse osmosis [4], and nanofiltration [5] are some of the removal processes. Biosorption is one of the widely used methods for the removal and the recovery of heavy metals from wastewater. Low cost, high efficiency, minimization, no additional chemical, regeneration, and metal recovery are some advantages of biosorption against to other removal process [6]. Algae [7], fungi [8], and yeast [9] are some of biomass materials used for biosorption studies. *Aspergillus* is a fungus widely used in biosorption studies. Several *aspergillus* species have been used for heavy metal ion adsorption such as niger [10], fumigatus [11], niveus [12], versicolor [13], flavus [14], terreus [15], and cristatus [16]. *Aspergillus tamarii* was used only textile dyes removal study [17].

Mechanism of biosorptions is classified as extracellular accumulation, cell surface sorption, and intercellular accumulation. Dead fungal cells sequester heavy metal ions through cell surface adsorption. Heavy metal ion uptake by surface adsorption is regardless of the surface functional groups such as carboxyl, amide, thiol, phosphate, and hydroxide [18]. The functional

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groups of *A. tamarii* were characterized by FTIR spectroscopy to find possible binding sites.

The objective of the present work was to find out the heavy metal ion adsorption capability of *A. tamarii*. For this purpose, dead biomass is treated with aqueous solution containing Cd^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} heavy metal ions by batch system. The effect of several parameters was studied. Treated heavy metal ion solution was analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) to monitor concentrations. The possible binding sites on the biomass involved in heavy metal ion complexation were evaluated by fourier transform infrared spectroscopy (FTIR).

2. Material and methods

2.1. Chemicals and instruments

All of the used chemicals were of analytical grade. The studied metal ion salts, $Cd(CH_3COO)_2$, $Ni(NO_3)_2{\cdot}6H_2O$, $MnCl_2$, $ZnCl_2$, and $Pb(NO_3)_2$ were purchased from Merck Chemicals. All the solutions were prepared with double distilled deionized water (Millipore 18 M cm^{-1} resistance). The pH of the working solutions was adjusted with 0.1 N NaOH (Merck) and 0.1 N HCl (Merck). Spectro Arcos ICP-OES is used to determine the concentrations of heavy metal ions in treated solutions. FTIR spectra of samples were measured with a Schimadzu IR Prestige-21 spectrometer.

2.2. Preparation of biomass

The fungus *A. tamarii* Kita MRC 72400 was obtained from the TUBITAK Marmara Research Center, Food Science and Technology Research Institute, Culture Collection Unit. The growth medium consisted of 50 g/L glucose, 2 g/L $NaNO_3$, 1 g/L KH_2PO_4, 0.5 g/L KCl, 0.5 g/L $MgSO_4{\cdot}7H_2O$, and 0.01 g/L $FeSO_4{\cdot}7H_2O$ for *A. tamarii* Kita MRC 72400. An aliquot amount of spores was transferred to previously autoclaved (121˚C for 15 min) 250 ml capacity erlenmeyer flask containing 100 ml growth medium and incubated at 30˚C and 120 rpm for three days. Harvested mycelium was autoclaved to obtain dead biomass, and filtered off and washed with double distilled water [19]. Finally, dead biomass was oven dried at 70˚C and then grinded in a mortar and stored at desiccator.

2.3. Biosorption experiments

The heavy metal solutions were prepared in mixture form containing 100 mL of 10 mg/L Cd^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+}. Biosorption experiments were carried out by adding 0.5 g dead biomass with rotary shaker at 50–200 rpm agitation rate for 10–200 min. The effect of initial pH on metal uptake was studied over pH range of 1.0–6.0. To study the effect of temperature on biosorption, the temperature of aqueous solutions was adjusted in the range of 20–50 ˚C. The heavy metal uptake efficiency with different initial concentrations was investigated in the range of 5–50 mg/L. The heavy metal concentrations in treated solutions were analyzed in ICP-OES after centrifugation at 800 rpm and filtration with 0.45 μm filter paper. The heavy metal uptake efficiency of biosorption was performed using the following formula:

$$R(\%) = \frac{C_0 - C}{C_0} \times 100 \tag{1}$$

where C_0 and C are the concentrations of heavy metals before and after biosorption in mg/L, respectively.

2.4. Characterization

FTIR analyses were performed with metal free and metal-loaded biomass. The samples were allowed to dry in vacuum oven at 25˚C and analyzed with ATR-FTIR.

3. Results and discussion

3.1. Effect of pH

pH is the most important parameter affecting biosorption of heavy metal ions onto *A. tamarii*. The net charge on biomass changes with ambient pH. At low pH values, active sites of biomass protonated and possible negatively charged binding sites decreased. In the high pH values, these sites are deprotonated and made available for binding [20]. To determine the functional groups of loaded and unloaded *A. tamarii*, biomass was analyzed by FTIR spectroscopy (Fig. 1). In unloaded spectrum, the peak around 3,271 cm^{-1} appeared due to O–H stretching. N–H stretching peaks were overlapped with this peak. The band at 1,741 cm^{-1} was attributed to the C=O group. The amide I and amide II peaks appeared at 1,643 and 1,547 cm^{-1} wavenumbers. The band at 1,373 cm^{-1} attributed to the asymmetric carboxyl stretching. C–N and C–O functional groups stretching bands overlapped at around 1,020 cm^{-1}. In loaded spectrum, no considerable differences were observed except from the peak at 950 cm^{-1} wavenumber. The presence of this new peak in loaded biomass was attributed to heavy metal ion–oxygen bond [21]. The results indicate that primarily –OH and –NH functional groups on biomass were affected by pH changes and heavy metal ion uptake occurred via these groups.

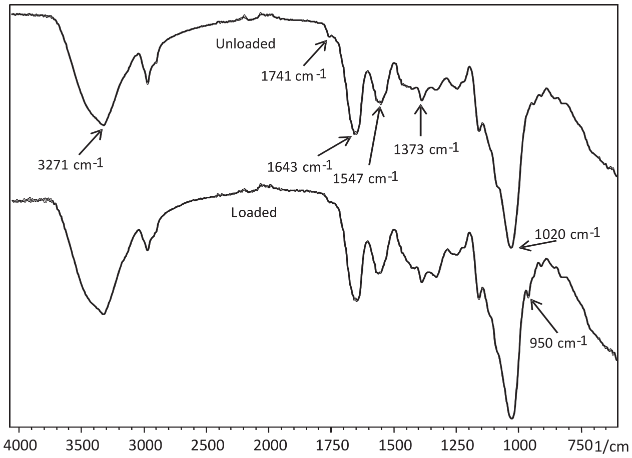

Fig. 1. FTIR spectra of unloaded and loaded biomass.

To investigate the effect of pH, biosorption studies were carried out in the range of 1.0–6.0. According to the results, it can be observed that the heavy metal ion uptake percentages are increased by raised pH values. At lower pH range, the surface of the biomass was covered by H^+ ion and positively charged surface caused to electrostatic repulsion between surface and metal ions. The competition between H^+ ion and heavy metal cations decreased by increased pH values and results in higher removal efficiency at higher pH ranges [22,23]. As can be seen from the Fig. 2, maximum removal efficiency was observed at around pH 6 for the studied heavy metal ions. Depending on the pH of the heavy metal ion solutions, complexation and ion exchange mechanisms took place during the experiments. Complexation mechanism occurred in the range of 1.0–4.0 pH values via –NH groups of biomass and best complexation observed at pH 2. Above pH 4, ion exchange mechanism occurred through H^+ ion and negatively charged groups of biomass and the heavy metal ion uptake percentages increased rapidly due to raised deprotonated groups of biomass [24]. The optimization experiments showed that the maximum removal efficiency was reached 27.89, 26.94, 32.21, 60.97, and 28.58% for Cd^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+}, respectively, by using 0.5 g biomass. According to the results, Pb^{2+} was the maximum adsorbed heavy metal onto *A. tamarii*.

3.2. Effect of contact time

Contact time influences the treatment efficiency of the biosorption process. The effect of contact time on the uptake of heavy metal ions was investigated in the range of 10–200 min and the results are given in Fig. 3. The heavy metal ion removal efficiency was reached 13.61, 13.01, 15.19, 40.49, and 10.82% for Cd^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+}, respectively, by using 0.5 g biomass in 10 min. Rapid uptake of Pb^{2+} ions occurred in 10 min than the other heavy metal ions. The equilibrium was reached in 150 min and after this time the removal efficiency of heavy metal ions did not change significantly. The rate of biosorption increased with rising contact time due to active sites of biomass and heavy metal ion interaction. After equilibrium, the removal efficiency did not significantly changed due to complete coverage of active sites [25].

3.3. Effect of agitation rate

The effect of agitation rate on the uptake of heavy metal ions was investigated in the range of 50–200 rpm in 150 min. As shown in Fig. 4, the removal efficiency increased from 18.25 to 27.89%, 14.31 to 26.94%, 20.17 to 30.02%, 43.83 to 60.97%, and 17.11 to 28.58% for Cd^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+}, respectively, by using 0.5 g biomass with increasing agitation speed from 50 to 150 rpm. Further increase in

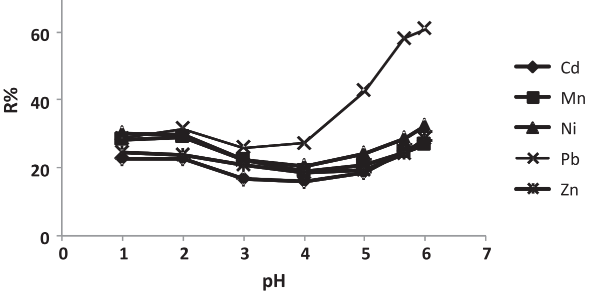

Fig. 2. Effect of initial pH on removal efficiency of heavy metal ions. $t = 150$ min; $C_0 = 10$ mg/L; $T = 25$°C; agitation rate = 150 rpm; biomass = 0.5 g.

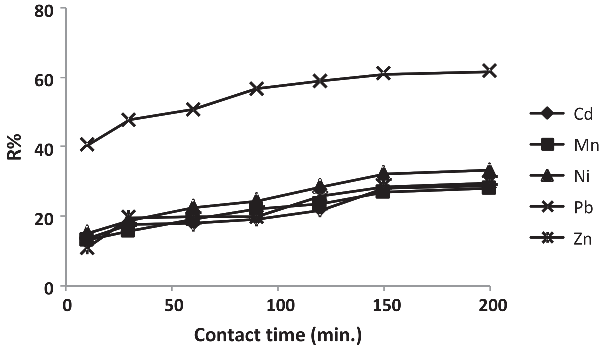

Fig. 3. Effect of contact time on removal efficiency of heavy metal ions. pH = 6; $C_0 = 10$ mg/L; $T = 25$°C; agitation rate = 150 rpm; biomass = 0.5 g.

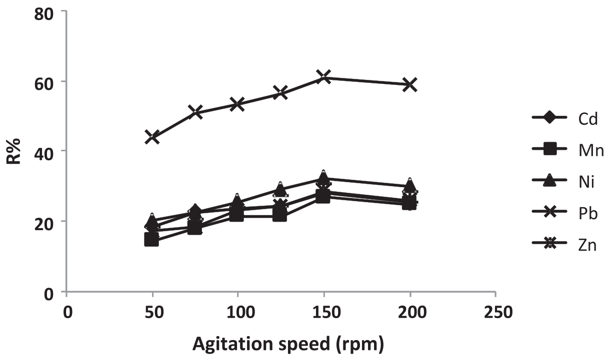

Fig. 4. Effect of agitation speed on removal efficiency of heavy metal ions. pH = 6; t = 150 min; C_0 = 10 mg/L; T = 25˚C; biomass = 0.5 g.

agitation speed resulted in a decrease of biosorption. The lower agitation speed decreased heavy metal uptake due to liquid film thickness around the particles but at higher agitation speed film diffusion rate increased and film resistance were eliminated [26]. At 200 rpm removal efficiency slightly decreased due to rapid reached equilibrium. In fact, rising agitation rate does not cause decreasing the removal efficiency. Rapid equilibrium causes quick coverage of active sites and decreasing the heavy metal uptake rate.

3.4. Effect of temperature

Temperature is a significant parameter for biosorption process. Fig. 5 shows the effect of temperature on the removal efficiency of heavy metal ions. The heavy metal uptake increased with elevating temperature from 20 to 25˚C. As temperature increased from 25 to 50˚C removal efficiency decreased to 24.21, 24.01, 30.76, 47.81, and 24.19% for Cd^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+}, respectively. At high temperature, the interaction rate between biomass and heavy metal ion decreased. The boundary layer is reduced with rising temperature and resulted in a decreasing removal rate of heavy metal ions [27].

3.5. Effect of initial concentration

The heavy metal solutions with different initial concentration were investigated in the range of 5–50 mg/L. Fig. 6 shows the effect of initial concentrations on heavy metal uptake efficiency. According to the results, removal uptake percentage was decreased with increased initial concentration by using 0.5 g of biomass. The heavy metal uptake efficiency decreased from 33.75 to 7.00%, 33.17 to 5.16%, 35.13 to 11.20%, 99.18 to 32.00%, and 33.69 to 1.94% for Cd^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+}, respectively, due to concentration increase from 5 to 50 mg/L. At low concentrations, possible heavy metal binding sites of biomass were available for quick binding. At higher concentrations decreased binding sites of biomass and slow diffusion of heavy metals to the biomass surface due to interparticle interactions caused to decreasing removal efficiency of heavy metal ions [28].

3.5. Effect of biomass dosage

The effect of biomass dosage on the biosorption of heavy metal ions is shown in Fig. 7. The biosorption of heavy metal ions increased to 51.69, 46.99, 58.74, 98.14, and 54.33% for Cd^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+}, respectively, with increased biomass dosage from 0.5 to 1.5 g. The uptake efficiency of Pb^{2+} ions was approximately constant which is higher than 1.5 g of biomass. The biosorption of other heavy metal ions did not reach the constant value in the range of 0.5–2.5 g of biomass. Pb^{2+} was selectively adsorbed

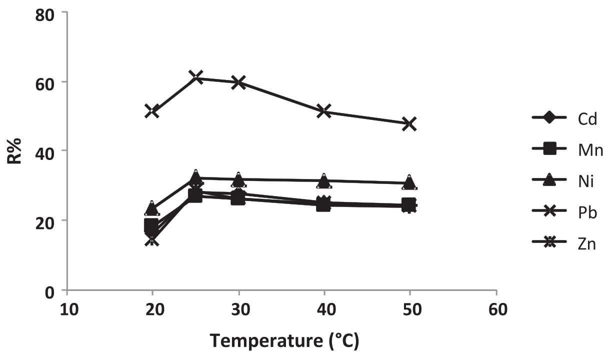

Fig. 5. Effect of temperature on removal efficiency of heavy metal ions. pH = 6; t = 150 min; C_0 = 10 mg/L; agitation rate = 150 rpm; biomass = 0.5 g.

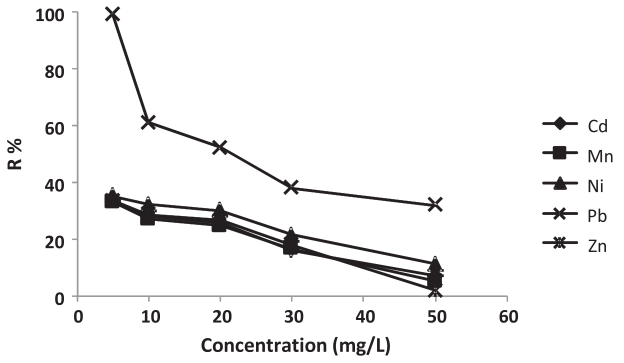

Fig. 6. Effect of initial concentration on removal efficiency of heavy metal ions. pH = 6; t = 150 min; T = 25˚C; agitation rate = 150 rpm; biomass = 0.5 g.

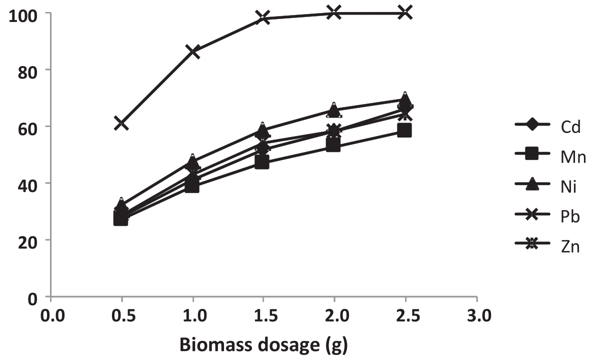

Fig. 7. Effect of biomass dosage on removal efficiency of heavy metal ions. pH = 6; $t = 150$ min; $T = 25$°C; agitation rate = 150 rpm; $C_0 = 10$ mg/L.

heavy metal ion by biomass and all Pb^{2+} ions in solution were adsorbed by 2.0 g of biomass. Other heavy metal ions continued binding to the uncovered active sites and resulted in increasing removal percentages.

3.6. Desorption of heavy metal ions

Desorption of adsorbed heavy metal ions from biomass was carried out on a rotary shaker at 150 rpm for 150 min by 0.1 M HNO_3. More than 90% of adsorbed heavy metal on the biomass could be recovered. The regenerated biomass can be used repeating adsorption–desorption cycle but the adsorption percentages decrease due to acid damage of the biomass.

4. Conclusions

According to the results, it is observed that Pb^{2+} is faster and more powerfully adsorbed heavy metal ion among the studied heavy metal ions by dead *A. tamarii* biomass. Cd^{2+}, Mn^{2+}, Ni^{2+}, and Zn^{2+} are weakly adsorbed by biomass. The biosorption affinity of *A. tamarii* biomass for the studied heavy metal ion is following the order $Pb^{2+} > Ni^{2+} > Cd^{2+} > Zn^{2+} > Mn^{2+}$. The obtained results showed that dead biomass of *A. tamarii* can be used for selectively removal of Pb^{2+} ion in aqueous solution and not effective for the removal of Ni^{2+}, Cd^{2+}, Zn^{2+}, and Mn^{2+} ions. The heavy metal ion uptake efficiency reached 98% for Pb^{2+} under the conditions of initial pH of 6, biosorption time 150 min, agitation rate 150 rpm, temperature 25°C, initial heavy metal concentration 10 mg/L, and biomass dosage 1.5 g. According to the FTIR results, heavy metal ion uptake occurs via –OH and –NH groups of *A. tamarii* biomass.

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