BIOSORPTION OF CADMIUM FROM AQUEOUS SOLUTION BY USING POWDERED DEAD OF ASPERGILLUS NIGER

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ABSTRACT
Aspergillus niger was isolated from wastewater of batteries factory in Baghdad, Iraq. Biosorption of cadmium from solution was studied using powder A.niger biomass. Biosorption experiment was conducted in 20ml of solution at 10mg/L initial concentration, with different pH (2, 3, 4, 5, 6, 7, 8) and variable temperatures (30, 35, 40), with contact times (1, 2, 3, 4, 5, 24 hr.) and pretreated fungal biomass (0.1g). Optimum conditions were selected for biosorption uptake onto fungi biomass. The best pH was found to be 6 for Cd(II). The optimum temperature was found to be 40 °C for Cd(II) ions. The optimum contact time was found to be 3 hr for Cd(II). The results indicated that fungi have high ability to removing cadmium.

KEYWORDS: Biosorption, Cadmium, Aspergillus niger.

INTRODUCTION
The removal and recovery of toxic heavy metal ions from wastewaters is of great importance from an environmental viewpoint, According to the ranking of metal interest priorities referred by Volesky, 2001[1], Cd(II) the most interesting heavy metals for removal and/or recovery considering the combination of environmental risk and reserve depletion.

Cadmium is one of the toxic heavy metals with a greatest potential hazard to humans and the environment. It causes kidney damage, bone diseases and cancer. Chronic exposure to elevated levels of cadmium is known to cause renal dysfunction, bone degeneration, liver damage.[2] The major sources of Cd (II) release into the environment through wastewater streams are electroplating, smelting, paint pigments, batteries, fertilizers, mining and alloy industries.[3] Therefore, there is a need for some alternative technique, which is efficient and
cost effective. Biosorption, based on living or nonliving microorganisms or plants, could be such an alternative method of treatment. It has distinct advantages over conventional methods of treatments, Biosorption of heavy metals from aqueous solutions is a relatively new technology for the treatment of some industrial wastewaters. It is defined as the accumulation and concentration of pollutants from aqueous solutions onto biological materials, thus allowing the recovery and/or environmentally acceptable disposal of pollutants.[4]

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 wall.[5]

MATERIALS AND METHODS

Preparation of metal ion stock The stock solution was prepared by dissolving the required amount of analytical grade 3CdSO4.8H2O (minimum purity 99 %) in distilled water to obtain a concentration of 1000 mg/L. Further dilutions were carried out during the course of the experiments to obtain different concentrations as desired.

Growth of fungal biomass Aspergillus niger previously isolated and identified from wastewater of batteries factory in Baghdad by serial dilution methods.[6] The fungus was cultured on potato dextrose agar at 28°C. The isolates were maintained on potato sucrose agar slants incubated at (25ºC) and then stored at (5ºC). The inoculation was made from 3-5 days old cultures under sterilized conditions.[7]

Preparation of the biomass for removal studies

For biomass preparation the isolated fungus was grown in potato dextrose broth at pH= 5, After 72h of growth, Biomass was harvested by filtration at the end of the fermentation process it was killed by autoclaving at 121°C for 30 min, washed thoroughly with distilled water and dried in an oven at 50°C for 24 hr. in a glass Petri plates, ground with mortar and pestle to make the powder biomass to particles and sieved by sieve size 1.18 mm (No. 16), This powdered biomass was used in further biosorption experiments.[8,20]

Biosorption studies

Cadmium uptake was done in Erlenmeyer flask (100 ml) containing 20 ml of the desired concentration at different parameter in rotary shaker at 150 rpm. These conditions were
maintained for all the experiments except as otherwise indicated. In all the studies the amount of viable biomass was 0.1 g powdered dead fungal biomass.

Biosorption experiments were repeated using *A. niger* to study the effect of some factors such as contact time, pH, temperature on the biosorption of Cadmium ion from the polluted water.

**Optimization of parameters**

All experiments were performed to study the effect of different factors such as pH, temperature, contact time, to the biosorption process of metal ions by *A.niger*.

**pH**

In this study, the experiments were conducted to study the effect of pH. The tested solutions 10 mg/L metal ions and dead biomass of *A.niger* 0.1g/20 ml Cd2+ metal solution were adjusted at pH 2, 3, 4, 5, 6, 7, using HCl or NaOH and left for 5 hr. on rotary shaker incubator at 30°C.[16]

**Temperature**

The optimal temperature value of *A.niger* for biosorption of heavy metals was determined at varied temperature of (30°C, 35°C and 40°C) by controlled rotary shaker incubator for 5 hr. at 150 rpm. This factor was examined in 10 mg/L metal ions and 0.1 g of dead biomass of *A.niger* /20 ml Cd2+ metal solution.[17]

**Contact time**

Samples were tested at 1, 2, 3, 4, 5 and 24hr. intervals during the biosorption experiments and analyzed for Cd (II).This factor that influence time was examined in 10 mg/L metal ions and 0.1 g of dead biomass of *A.niger* /20 ml.[17] Amount of heavy metals biosorbed by *A.niger* biomass after a specific contact time was calculated from the difference between the total amount of heavy metal added and that residual in the supernatant after treatment. The percentage of metal removal was calculated.

**RESULTS AND DISCUSSION**

**Preparation of Biosorbents**

Non-living dried fungal biosorbent of species *Aspergillus niger*, it can be described as a soft texture and its black color. (Fig.-1).

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The effect of pH on biosorption

The statistical analysis for *A. niger* showed the mean biosorbed concentration of Cd was significantly influenced (P<0.05), by the different pH and higher mean biosorbed concentration was recorded at pH 6 was 5.7 mg/L, while the lowest concentration was observed at a low pH is pH 2 was 1.3 mg/L. This is due according to[10] Most of the microbial surfaces are negatively charged due to the ionization of the functional groups, thereby contributing to metal binding. The pH of the biosorption medium affects the solubility of the metal ions and the ionization state of the functional groups. Fungal surfaces have a negative charge in the pH range of 2-6. Biosorption of heavy metals observed in *A. niger* biomass was high removal efficiency 57% at pH 6 (Fig.-2). The decreased metal biosorption was observed at very low acidic pH of 2.0 and 3.0. The biosorption ability of *A. niger* was decreased with increased in pH to 7 and above. The study results was conflicted with[15] that showed the optimum biosorption of cadmium ion by *Aspergillus niger* was obtained for a pH ranging between 4.0 and 5.5. This range was selected for the experimental design.

Figure (2): The removal efficiency(%) for cadmium by *A. niger* at different pH values.
The effect of temperature on biosorption

The range of temperature values (30-35–40 °C) was used to determine the optimum temperature removal of heavy metals.

The statistical analysis for *A. niger* showed the mean biosorbed concentration of Cd was significant different (P<0.05), at temperatures of 30, 35 and 40.

In current study showed the mean of heavy metal concentration biosorbed by *A. niger* at different temperatures. It is very clear that highest capacities were recorded for Cd under test at 40º C (Fig.3). For cadmium biosorbed concentration, the mean was varied from 5.8 ± 0.07 mg/l to 7.0 ± 0.12mg/l. All these data were found at temperatures was increase in biosorption capacities was seen for all metals at 40º C.

![Figure (3): Mean metal biosorbed for cadmium by *A. niger* at different temperature.](image)

Temperature is one of the factors which may affect the sorption efficiency above the range of 35 C° however biosorption increases with the increase in temperature.[11]

The biosorption that related to increased temperature would be reflected to the enhancement of functional groups at the surface of the adsorbent where more hydrolysis of the surface occur at higher temperatures, while the decrease in adsorption value after 50° C that inferred to increase temperature in the system that will result in movement increase of the adsorbate species, and this means that particles may travel at a faster rate to the surface to get adsorbed.[18] In addition, the adsorbed biomass might have enough energy from temperature of the system and subsequently be desorbed at even a faster rate than adsorption rate.[19] In present study the effect of temperature revealed the increase in biosorption with the increase
in temperature due to the increased collision frequency between sorbate and sorbent. And this results was agreed with.\textsuperscript{[12]} \textsuperscript{[13]}(Santhi and Jagadeeswari, 2015) that similar with study results, that found the dead biomass of fungi \textit{Aspergillus niger} was evaluated and optimized of biosorption which showed optimal temperature at 40°C.

The effect of contact time on biosorption

(Table 1) The statistical analysis for \textit{A.niger} in showed a significant difference for different contact time (P<0.05), at 3 hours and higher significant at 4 and 5 hours and less significant at 1 and 24 hours, for Cd(II) The fungi species \textit{A.niger} the results was indicated the higher removal efficiency was observed 8.0 ± 0.22 with Cd at 3 hr. Contact time is one of the important parameters for successful use of the biosorbents for practical application and rapid sorption is among desirable parameters.\textsuperscript{[23]} The study results was conflicted with\textsuperscript{[14]} that showed the maximum removal efficiency percentage uptake of cadmium ion by culture fungi at 2 hours.

<table>
<thead>
<tr>
<th>Contact time</th>
<th>Mean metal biosorbed concentration (mg/L) ±SD</th>
<th>LSD value</th>
<th>Efficiency(%) Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 hr.</td>
<td>4.8 ± 0.01</td>
<td>1.18 *</td>
<td>48</td>
</tr>
<tr>
<td>2 hr.</td>
<td>6.05 ± 0.13</td>
<td>1.53 *</td>
<td>60.5</td>
</tr>
<tr>
<td>3 hr.</td>
<td>8.0 ± 0.22</td>
<td>1.25 *</td>
<td>80</td>
</tr>
<tr>
<td>4 hr.</td>
<td>6.64 ± 0.11</td>
<td>1.42 *</td>
<td>66.4</td>
</tr>
<tr>
<td>5 hr.</td>
<td>6.9 ± 0.25</td>
<td>1.19 *</td>
<td>69</td>
</tr>
<tr>
<td>24 hr.</td>
<td>5.8 ± 0.11</td>
<td>1.37 *</td>
<td>58</td>
</tr>
<tr>
<td>LSD value</td>
<td>1.47 *</td>
<td>1.62 *</td>
<td>----</td>
</tr>
</tbody>
</table>

* (P<0.05).

In another research, 0.7 g/l of fungal biomass of \textit{Aspergillus niger} showed 84% removal of cadmium ions.\textsuperscript{[21,22]} while in this study, 0.1 g/20 ml of fungal biomass of \textit{Aspergillus niger} showed 80% removal of cadmium ions.

CONCLUSION

It can be concluded from the present investigation that \textit{A. niger} has efficient potential for the Cd metal uptake from solution. The optimal conditions were found to be pH 6, 3 hr., 40°C and it was noted that biosorption increased with the increase in temperature. Biosorption of Cd(II) ions was exothermic and the physical mechanism plays a major role in the biosorption processes. The negative charge of fungi biomass (when pH= 5-6) became favorable to the attraction of positive heavy metals charges.
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REFERENCES