ABSTRACT

The aim of present work was to apply algae for metal removal from compost wastewater. The potential of alginate immobilized *Chlorella* to remove Cu\(^{2+}\) ions from compost wastewater was investigated in this study. The effect of initial metal concentrations and contact time on biosorption and removal efficiency of tested metals was investigated at original initial pH value of compost wastewater. Firstly, model sample solutions were prepared. We found out that Cu\(^{2+}\) ions could be removed by using alginate immobilized *Chlorella*.

*Keywords*: algae, compost wastewater, metal removal

INTRODUCTION

Because of their chemical characteristics, toxic effect and accumulation tendency in human body, heavy metals represent a serious hazard to human health. Several live organisms (e.g. algae, bacteria, fungi) have been investigated for metal sorption from polluted waters. Algae have proven to be very useful for this purpose due to their availability, low costs and the capability to uptake even large quantities of heavy metals. Cells of *Chlorella* were reported to be isolated from soil were highly resistant to heavy metals and were capable of taking up the heavy metal ions such as Cd\(^{2+}\), Zn\(^{2+}\) and Cu\(^{2+}\), respectively [1]. In another research, a series of batch experiments was conducted to compare the ability of several algal species including *Chlorella* in removing nickel and zinc from synthetic wastewater [2]. Physiological and morphological responses of lead or cadmium by *Chlorella* treatment were studied [3].

Different natural immobilisation media, such as alginites, chitosan, and cellulose derivatives have been used for algal cell immobilisation, while alginate is still one of the most frequently used carriers due to its advantages such as very simple preparation, biocompatibility and cost-effective immobilization. Otherwise, the cell immobilization may enhance sorption capacity, offers opportunity for biomass retention within the working environment, easy separation of products from cells and relatively high local cell density. The size of algal beads may also influence the metal removal efficiency of metals as well as other environmental parameters, such as pH and contact time, and initial metal concentration also play a great role in this process [4].

The main objective of this study was to explore the feasibility of alginate immobilized *Chlorella* for removing heavy metal ions Cu\(^{2+}\) from drinking and compost wastewater samples. The sorption capacities of the sorbent for the above mentioned metals were studied under various initial metal concentrations and different experimental conditions, such as pH and contact time.
MATERIALS and METHODS

Samples
Model water sample and compost wastewater were taken for analysis. Model solutions were prepared by dissolving 1 g/L of Cu in drinking water. Adequate solutions were prepared by diluting this standard Cu-solutions. Compost wastewater was taken from the local Industrial composting facility system.

Analytical methods
The parameters were determined according to the standard methods as seen from Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Apparatus</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td></td>
<td>Iskra pH meter</td>
</tr>
<tr>
<td>Conductivity</td>
<td>µS/cm</td>
<td>WTW conductivity meter</td>
</tr>
<tr>
<td>Turbidity</td>
<td>NTU</td>
<td>HACH Turbidymeter</td>
</tr>
<tr>
<td>Cu</td>
<td>mg/L</td>
<td>AAS</td>
</tr>
</tbody>
</table>

Several analyses were obtained in order to follow the experiment’s performance. The samples were filtered through filters (GF-3, Macherey-Nagel) in order to exclude most of the solids present in the water and diluted before analysis if necessary. The metal content in the solution was determined by an atomic absorption spectrophotometer (AAS, Perkin-Elmer, AAAnalyst 400). The calculations for metals were made according to the previously prepared calibration curve. The metal removed by algal beads was determined by subtracting the residual metal concentration from the initial metal concentration in the solution.

Materials
The cells of *Chlorella* were delivered from the local algal technology center (AlgEn, Slovenia) and cultivated in Bold’s Basal growth media at room conditions. After a 10-day cultivation when the microalgae were acclimatised, the algal cells were harvested by centrifugation (at 3500 rpm for 10 min). Immobilised algal beads were prepared by entrapping cells of *Chlorella* in an alginate matrix according to the following steps [5] (Ruiz-Marin): the harvested cells were re-suspended in distilled water to form a concentrated algal suspension, which was then mixed with 4% sodium alginate (Fluka) solution at a 1:1 volume ratio to yield a mixture of 2% algal alginate suspension. The mixture was then dropped into a 2% calcium chloride (Merck) solution using a 25 mL burette. The drops of algal alginate solution gelled into small beads (with cell numbers of around 6.6x10^5 cells bead\(^{-1}\)) upon contact with calcium chloride solution (2%). The solution was stirred to prevent aggregation of the algal cell entrapped in alginate beads. Immobilised algal beads were then stored in a calcium chloride solution for approximately 4 h, rinsed with saline solution (0.85% NaCl) and subsequently with distilled water. The beads were then transferred to the algal growth medium and were incubated under room conditions for 3 days. After short incubation, the beads with immobilised algal cells were removed from the medium and washed twice with saline solution (0.85%) and finally with distilled water. The beads are seen from Figure 1.
Figure 1: The alginate beads with algae

The experiments were performed by *Chlorella* immobilized algal beads placed into glass jars with drinking water. For the experiments with metals, the drinking water was spiked with Cu solutions in adequate concentrations in order to achieve concentrations of 25, 40, 80 or 150 mg/L of Cu ions.

**RESULTS**

The pH effect was studied in the range of 3-7 at initial metal concentration of 25 mg/L. The removal capacities of copper increases with pH up to 5, but it must be considered that at pH values higher than 6 the precipitation effect was observed, more obvious at pH 7. The maximum efficiency for Cu$^{2+}$ ions was calculated at 20.24 mg/g (98.86%). This is in accordance with the previous investigations which shown increased metal sorption with increasing pH of the solution [6]. It could be explained by the fact that the increase in the initial solution pH will result in the increase of the dissociation degree of functional groups from sorbent surface, and consequently, the number of electrostatic interactions will increase. The pH was set to 5. The contact time for successful metal removal was tested by using *Chlorella* immobilised algal beads. The contact time was 20, 40, 60, and 180 mins. The initial and equilibrium concentration of Ni was determined. It was found that contact time is around one hour (60 min). The data obtained are presented in Table 2.

Table 2. Influence of contact time in model solution (initial c= 25 mg/L)
In order to study the effect of initial metal concentration on sorption capacity by alginate immobilised *Chlorella*, the experiments with different concentrations of Cu\(^{2+}\) ions in the sorption medium were performed, wherein the initial metal concentrations were varied in the range of 25–150 mg/L. Results are presented in Figure 2.

![Figure 2: The sorption capacity as function of equilibrium concentration for Cu\(^{2+}\)](image)

The sorption capacity of metal ions increased with increase in initial metal concentration, whereby the equilibrium metal concentration also increased. Higher initial concentrations provide the driving force to overcome mass transfer resistance of metal ion between the aqueous solution and solid, thus increasing the metal uptake. In addition, increasing initial metal ion concentrations also increases the number of collisions between metal ions and sorbent, which enhances the sorption process. However, the experimental maximum biosorption capacities obtained in biosorption of Cu\(^{2+}\) ions by alginate immobilised *Chlorella* cells were found to be 150.07 mg/g.

Table 3 represents the measurement for determining removal efficiency in compost wastewater. The presence of organic compounds has some influence on copper removal since all measured values of Cu-ions were lower compared with model samples. However, pH value 5 is better than higher values. Turbidity was measured at 1000 NTU and conductivity
22 mS/cm. The values are around 1000 times higher as in drinking water samples, which is the reason for the lower efficiency due to hindrance.

Table 3. Determination of Cu removal from compost wastewater

<table>
<thead>
<tr>
<th>t(min)</th>
<th>pH</th>
<th>Cu (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>5</td>
<td>45.6</td>
</tr>
<tr>
<td>20</td>
<td>6</td>
<td>27.9</td>
</tr>
<tr>
<td>60</td>
<td>5</td>
<td>68.1</td>
</tr>
<tr>
<td>60</td>
<td>6</td>
<td>62.2</td>
</tr>
<tr>
<td>180</td>
<td>5</td>
<td>76.3</td>
</tr>
<tr>
<td>180</td>
<td>6</td>
<td>64.2</td>
</tr>
</tbody>
</table>

CONCLUSION

- Alginate immobilised *Chlorella* is efficient for removing Cu$^{2+}$ ions from water.
- The capacity by alginate immobilised *Chlorella* cells were found to be 150.07 mg/g Cu$^{2+}$ ions.
- In compost wastewater the removal efficiency decrease due to organic compounds content which hinder Cu-ions uptake by alginate beads.

LIST OF REFERENCES