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Metal removal studied by a laboratory scale immobilized microalgal reactor *

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Abstract—A laboratory scale algal column reactor packed with 75 ml alginate-algal beads was used to treat 30 mg/L Cu and Ni with a HRT of 30 minutes. At the end of loading 4L metal solution, over 97% of Cu and 91% of Ni were removed from the wastewater with a final residual of 1.76 mg/L Cu and 8.8 mg/L Ni. Up-flow was preferred to down-flow in maintaining a constant flow rate and hence HRT. Amount of metal recovered during regeneration depended on concentration and nature of regenerant used. Dilute acid was a better regenerant than calcium in terms of metal recovered (90%) and volume needed for regeneration. The consistency in the metal removal performance by the algal column over 10 metal treatment and regeneration cycles suggested that the algal beads can treat Cu or Ni bearing wastewater over 400 times its own volume.

Keywords: immobilized microalgal reactor; industrial wastewater treatment; metal.

1 Introduction

Industrial wastewaters, particularly those discharged from manufacturing of printed circuit board (PCB) and electroplating contain large amount of toxic heavy metals, particularly copper (Cu) and nickel (Ni). Existing techniques such as chemical precipitation, membrane processing and ion exchange in treating metal containing wastewaters are either too expensive in initial set up and consumable or having problems in the final sludge disposal and regeneration of resin beds. In order to meet the more and more stringent discharge requirement, comparative cheap and effective alternatives should be exploited to treat the metal bearing wastewaters. Microbial (bacterial, fungal and algal) mass had been reported (Kapoor, 1995; Cho, 1994; Sag, 1996) to have high metal sequestering ability through their active metal uptake and accumulation inside the cell as well as the biosorption of the metals by anionic groups associated with the cell wall components (Volesky, 1990). Our laboratory had shown that *Chlorella vulgaris*, an unicellular green alga with a cell diameter of 5μm, had a very high Cu and Ni uptake ability. In facilitating the reactor design for industrial purpose and avoiding the separation process of the mass of algal suspension from the liquid medium, the algal cells were immobilized with sodium alginate, a polysaccharide gel matrix, in

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form of spherical beads with 3 to 4 mm diameter. A laboratory scale column reactor packed with alginate-algal beads was studied for its Cu and Ni removal efficiencies. This experiment was carried out in parallel to a larger pilot scale study using 20—40 L PVC bioreactors. The integrity of the algal column for cyclic operation with respect to factors such as flow direction and regeneration were also investigated.

2 Materials and experiments

2.1 Algal mass culture

The unicellular green alga, *Chlorella vulgaris* from Carolina Biological Supply was mass cultured in commercial Daunta Medium with average light intensity of 5000 lx at a light-dark cycle of 14 to 10 hours in 20L transparent carboys. The culture was aerated with filtered air at a temperature of 22 ± 1℃. Algal cells were harvested at a density of 8 to 9×10^7 cells ml^{-1} through centrifugation (10000 r/min for 10 minutes). The cell slurry collected was ready for immobilization.

2.2 Immobilization of algal cells with sodium alginate

Immobilization of the algal cells in sodium alginate solution followed the method of Tam *et al*. Spherical algal beads with final 4% gel concentration was obtained by extruding the alginate-algal mixture through 1 mm i.d. Teflon tubing by means of peristaltic pump into 3% $CaCl_2$ solution for gel setting and curing. In this way, algal beads of average 3 to 4 mm diameter were formed with a cell density of 5.6×10^6 cells/bead.

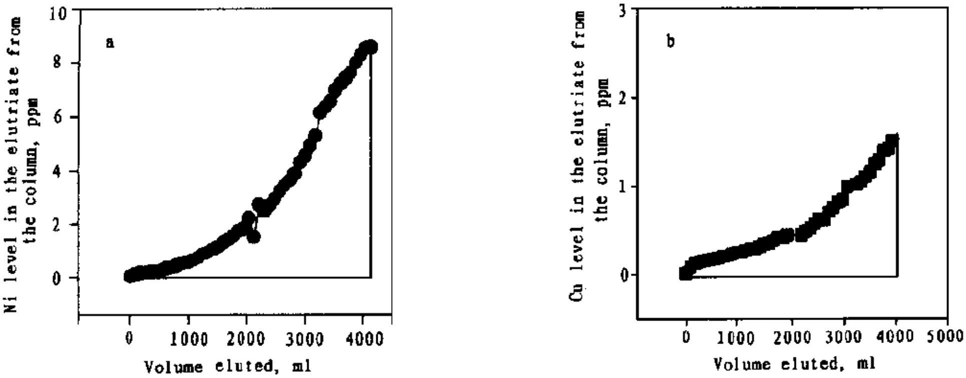
2.3 Laboratory scale algal column reactor studies

An Econo column, i.d. 25 mm and length 200 mm with an approximate volume of 100 ml, was packed with 75 ml alginate-algal beads. The column reactor was fed with 4L 30 mg/L Cu (from $CuSO_4$) or Ni (from $NiCl_2$) metal solution in either down-flow or up-flow direction. The hydraulic retention time (HRT) was maintained at 30 minute by fixing the flow rate (2.5 ml/min) of the metal solution through the column by a peristaltic pump. Effluent from the column was collected in an auto-sampler with 8.8 ml per tube. The Cu and Ni content was assayed in every ten tubes by flame atomic absorption spectrophotometer (Hitachi model Z8200). At the end of metal feeding, the algal column was regenerated with either calcium or dilute HNO_3 solution (2% v/v). After the regeneration process, the column was washed with 200 ml distilled water. A second treatment-regeneration cycle was started and the process continued.

3 Result and discussion

3.1 Metal removal efficiency by the algal column

Fig. 1a and Fig. 1b show the Ni and Cu removal efficiency by the algal column, respectively. From the initial 4L 30 mg/L metals, over 97% of the Cu and 91% Ni loaded was taken up by the algal beads with a residual 1.76 mg/L Cu and 8.0 mg/L Ni in the effluent at the end. The results showed that algal beads had a stronger binding affinity for Cu than Ni. This is probably related to the fact that Cu is an essential element for normal algal growth and hence the cell surface possesses ligands or specific groups in holding Cu for assimilation. These working profiles provide means in assessing the working volume or time of the algal column with respect to the discharge limit required and hence information on working life of the column for regeneration. Thus, if the discharge limit for nickel is 2 mg/L, the working volume would be 1880 ml and the corresponding working life well be 12.5 hours.



Total Ni input: 120 mg
Amount of Ni discharged: 11.76mg(9%)
Ni removed by the algal column: 108.24mg (91%)

Total Cu input: 120mg
Amount of Cu discharged: 2.61mg(2.2%)
Cu removed by the algal column; 117.39mg (97.8%)

Fig.1 The nickel (a) and copper (b) removal efficiency by the algal column

3.2 Effect of flow direction on column integrity in cyclic operation

The consistency in the treatment efficiency of a system is one of the major concerns in industrial application. This implies that a fairly constant flow rate or HRT is expected throughout the working life of the column. The flow rate in the algal column, however, was much affected by the flow direction. The result is summarized in Fig.2. In an up-flow mode operation, the performance of the algal column was highly consistent between the first and second cycle of operation with the flow rate maintained at 2.46 ml/min at the end of the second cycle of operation. This was not much different from the initial 2.5 ml/min. However, with a down-flow mode operation, the Ni removal performance for the first 2000 ml was similar to that of the down-flow operation but a better Ni removal was recorded at the end of the first cycle with a residual of 4.1 mg/L Ni which was half that of the up-flow operation. Associated with the better removal efficiency was the reduced flow rate to 2.0 ml/min. The column performance in the second cycle of treatment was also much better than the first one. Despite that a similar final 4.0 mg/L Ni as the first cycle was recorded at the end, much less Ni was discharge in the effluent in the first 3500 ml (Fig.2). The improved metal removal performance was concomitant with a greater reduction in the flow rate to 1.67 ml/min at the end of the second cycle. The reduced flow rate was due to greater resistance to the flow as the downward hydraulic pressure of the metal solution on the algal beads packing them more close to each other. The reduction in flow rate increased the HRT of the metal solution in the column and hence accounted

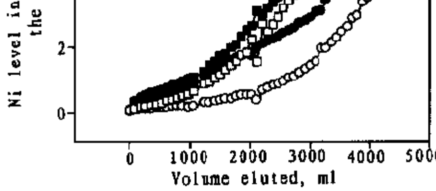


Fig.2 Effect flow direction on Ni removal by the algal column

for the better Ni removal. The up-flow mode operation was preferred due to its consistency and hence a better control in cyclic operations at the compensation of lower metal removal efficiency.

3.3 Column regeneration and reusability

Calcium was tested as regenerant for dual purposes, regeneration and re-strengthening of the algal beads since calcium is used as curing agent in the immobilization process. The metal recovered by calcium depends on the concentration used (Fig. 3a). The more concentrated the calcium used, the smaller volume with more concentrated Ni to be recovered. However, dilute HNO_3 (2% v/v) appeared to be a more competent regenerant than Ca (Fig. 3b) and over 90% of the adsorbed Ni can be recovered in about 400 ml. This is equivalent to a volume concentration factor of 10 for the metal.

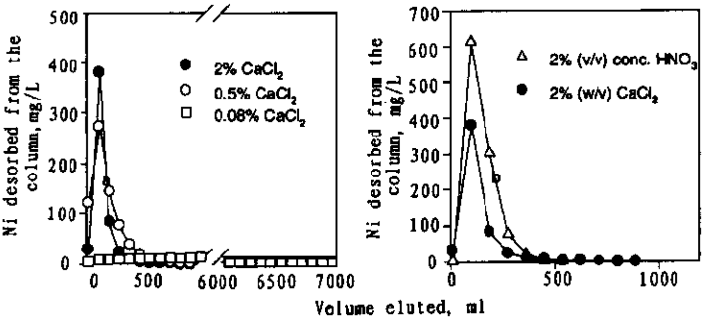


Fig. 3 Regeneration with $CaCl_2$(a) and HNO_3(b)

The reusability or durability of the algal column was tested with repeated cyclic operation after regeneration process. Fig. 2 shows an example of Ni removal (2nd cycle, up-flow) after the regeneration, the Ni removal performance was highly consistent with the first cycle as discussed before. In other words, the efficiency of the algal column was retained after the regeneration process. Fig. 4 shows a summary result on cyclic performance (3 cycle of treatment, *T*-regeneration, *R*) on treating Cu solution by the algal column. Results also demonstrated that the Cu removal performance was not affected after regeneration. At the time of this reporting, 10 treatment-regeneration cycles had been completed with the algal column not loosing its metal removal capacity after regeneration. This implies that a volume of the algal beads can treat, at least, a total of 400 times its volume of Cu or Ni bearing wastewater. The life span of a batch of the algal beads was now under testing.

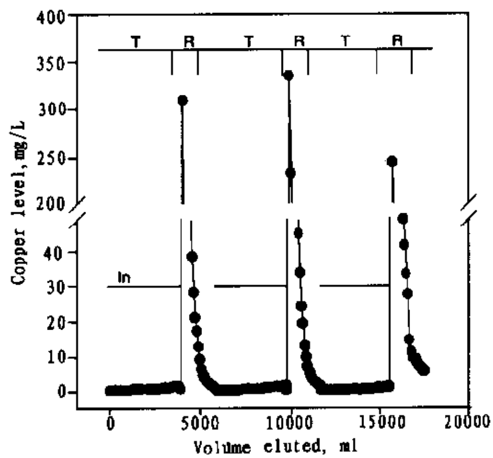


Fig. 4 Summary of the cyclic performance on Cu removal (*T*) and column regeneration (*R*) with a loading of 4L 30 mg/L Cu solution (*In*)

4 Conclusion

The laboratory scale alginate immobilized Chlorella vulgaris column demonstrated a high Cu and Ni removal capacity from the metal solution. The integrity of the algal column was better with respect to maintaining a constant flow rate, hence a constant HRT in up-flow than down-flow operation. Dilute acid was a better regenerant than calcium in terms of concentration and volume of metal recovered. After regeneration, the algal column can be reused without loosing its metal removal efficiency.

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