Recovery of Heavy Metals using Oxidized *Undaria pinnatifida* in Plating Wastewater

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Abstract

Biosorption process is an economic and potential process for metal sequestering from the water. The oxidized *Undaria pinnatifida* by nitric acid had high uptake capacity for heavy metals of 4 - 6 meq / g dry mass. For the application of oxidized *Undaria pinnatifida*, recovery of metal in plating wastewater was studied. The uptake capacity of the oxidized *Undaria pinnatifida* was high compared to the ion exchanger IR-120 plus. The treatment efficiency of chromium and copper in the wastewater was 85% in batch. Activated carbon was used to assist the recovery of water by removing organic matters of the wastewater.

Introduction

The plating wastewater was chosen as a model process, because it had many kinds of metal and most plating industries in Korea were small scale that wanted to reduce their waste treatment cost. Plating wastewater contents are heavy metals, various organic materials, and cyanide. Problems of plating wastewater are the production of sludge containing much water and heavy metals which needs extra treatment and high operating cost due to chemicals in both a precipitation and a flocculation process. Biosorption process has advantages compared to other processes such as cheap cost of materials, easiness of operation and selectivity over the alkaline metals[1]. Biosorbent which had high uptake capacity by chemical modification was developed and applied to the plating wastewater to reuse water, to recover heavy and precious metals, and to develope economic treatment process[2].

Materials and Methods

Undaria pinnatifida was harvested from west sea. The cells were collected as a

fine powder by drying, grinding and filtering with a 100-mesh sieve. The procedure of chemical modification was as followed. 10g of *Undaria pinnatifida* was oxidized in 20%, 200 ml nitric acid at 100℃. The treatment time was 3 hours. It was rinsed thoroughly by 200 ml of water 5 times. After being dried at 50℃, it was stored in a refrigerator for future work. Wastewater were obtained from the plating factory in Ansan, Korea and kept in room temperature for the future work. The procedure of biosorption experiment was as followed. Predetermined biosorbent was put to the given amount of wastewater, then mixed in a shaking incubator at 30℃. After pH adjustment using 0.1M HNO_3, NH_4OH and NaOH, the solution was centrifuged at 10,000 rpm for 20 min to remove suspending biosorbent, then metal concentration of the supernatant was analyzed using AA (Atomic Absorption spectroscopy : Perkin-Elmer, USA). Activated carbon was purchased from Sigma-aldrich(USA) and the procedure of adsorption was same as that of oxidized *Undaria pinnatifida*. COD was measured using COD bottle and kit of HACH(German).

Results and Discussion

An uptake capacity of an oxidized *Undaria pinnatifida* for each wastewater without any pre-treatment was very low, as was expected, because of low pH of the solution and chelating agent in the solution. The pH of chromic wastewater and acd-alkaline wastewater was changed using NH_4OH and NaOH and the chelating agents in the chelate wastewater were oxidized using $KMnO_4$ and HNO_3 to degrade it. After pre-treatment, the uptake capacities of heavy metals in each wastewater were increased.

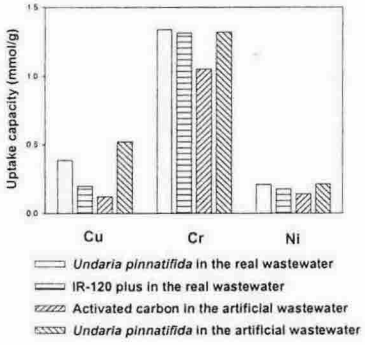

Fig. 1. Uptake capacity of oxidized *Undaria pinnatifida*, ion-exchanger and activated carbon in the chromic plating wastewater

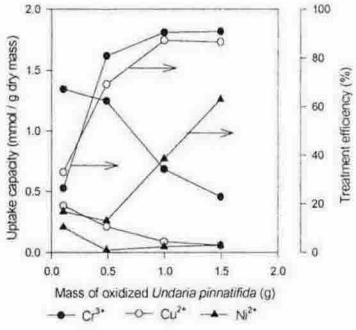

Fig. 2. The uptake capacity of the oxidized *Undaria pinnatifida* by the variation of weight of biosorbent in the real plating chromic wastewater. total solution volume : 100 ml

To test the capability of oxidized *Undaria pinnatifida* in the real wastewater, the comparison of uptake capacity at each wastewater between oxidized *Undaria pinnatifida* and ion exchanger IR-120 plus was performed. One of the results among them was shown in Fig. 1 and this result showed the superiority of oxidized *Undaria pinnatifida* at most kinds of heavy metals in the wastewater. The artificial wastewater, whose concentrations of heavy metals were same as in the real wastewater but other components were not included to exclude other effects on the uptake capacity of heavy metals, were made for the blank test.

Fig. 2 showed the uptake capacity and the treatment efficiency of oxidized *Undaria pinnatifida* in changing the weight of biosorbent. As was expected, the uptake capacity decreased while the weight of biosorbent increased due to the relative large proportion of the biosorbent compared to the adsorbate and total treatment efficiency increased.

The component of real wastewater includes lipid, surfactant, chelating agent etc. and these components may interfere with the treatment of wastewater using biosorbent. Although direct application of oxidized *Undaria pinnatifida* to the treatment of plating wastewater showed the good treatment efficiency, the development of method for treating the organic compounds in water was demanded to recover process water together with metals. Activated carbon is used to remove organic matter in wastewater and this process not only doesn't need another capital cost but also doesn't make overall process complicated because it is similar to the biosorbent process. The uptake capacity of activated

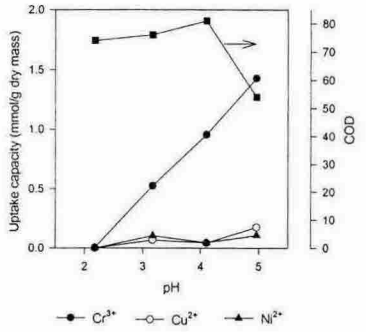

Fig. 3. The uptake capacity of the activated carbon by the variation of solution final pH in the real plating chromic wastewater.
initial COD : 150 ppm
mass of activated carbon : 0.5 g total solution volume : 100 ml

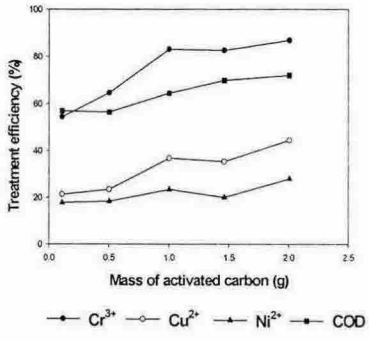

Fig. 4. The treatment efficiency of the activated carbon by the variation of weight of adsorbent in the real plating chromic wastewater.
initial COD : 150 ppm
final pH : 4
total solution volume : 100 ml

carbon in the artificial plating wastewater was studied and one of the results was shown in Fig. 1. This figure revealed the fact that activated carbon has high uptake capacity for the chrome in chromic wastewater and relatively low uptake capacity for the Cu^{2+} and Ni^{2+}. In mixed heavy metals system, metal having high charges shows higher uptake capacity than that having low charges. For the pretest of applicability of activated carbon, its adsorption capacity of metal and organic matter was determined in the real wastewater. Fig. 3 showed the effect of solution pH on the removal efficiency of metals and COD. The point worthwhile attention was high uptake capacity of activated carbon for the Cr^{3+} and low COD value at pH 5. The removal efficiency for the Cr^{3+} was similar to that of oxidized *Undaria pinnatifida*. Low COD value at pH 5 was thought that the precipitate of metal occurred at that pH could remove organic component. The change of COD value caused from the metal itself and chelating agent was corrected through independent experiment. From Fig. 4 showed the effect of the mass of activated carbon on the removal of COD and metals. Though overall profile was similar to that of oxidized *Undaria pinnatifida*, the removal efficiencies of Cu^{2+} and Ni^{2+} were lower than those of the oxidized *Undaria pinnatifida*.

Several experiments related to activated carbon showed the positive aspects in removing metal and organic material. Thus, the experiments for the effects of both the oxidized *Undaria pinnatifida* and the activated carbon were studied. Fig. 5 showed the effect of both adsorbent on the removal of heavy metals in the wastewater.

References

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2) Park, J. Y. C. Chun, and Y. J. Yoo, "Characteristics of metal biosorption of oxidized Undaria pinnatifida"(1999), J. Microbiol. Biotechnol. 9(5), 650-654.

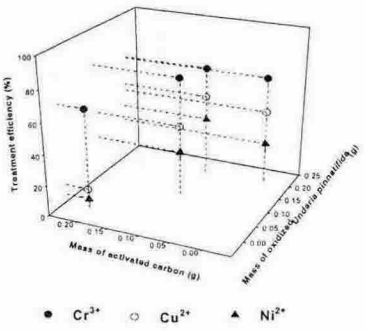

Fig. 5. Uptake capacity of heavy metals in the chromic wastewater using oxidized *Undaria pinnatifida* and activated carbon.
final pH : 4