Korean J. Chem. Eng., **18**(6), 955-960 (2001)

Removal of Heavy Metals in Plating Wastewater Using Carboxylated Alginic Acid

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(Received 7 February 2001 • accepted 4 July 2001)

Abstract−Potentially, biosorption is an economic process for metal sequestering from water. Carboxylated alginic acid showed high uptake capacities for heavy metals of 5-6 meq/g dry mass. For application to actual plating wastewater, the carboxylated alginic acid was immobilized using PVA. In order to remove chelating or organic materials in plating wastewater, oxidation using sodium hypochlorite was performed as a pretreatment. When carboxylated alginic acid bead was applied in a packed-bed contactor, the breakthrough point of copper ion in the acid-alkaline wastewater appeared around 350 bed volumes; the breakthrough point of nickel ion in the chelating wastewater emerged around 200 bed volumes. The adsorption capacity for heavy metal of the carboxylated alginic acid bead was higher than that of a commercial ion exchanger (IR-120 plus) in plating wastewater.

Key words: Alginic Acid, Plating Wastewater, Heavy Metal, Biosorption

INTRODUCTION

Components of plating wastewater are mainly heavy metals, various organic materials, and cyanide. Until now, alkaline-chlorination and chemical precipitation methods for treatment of cyanide and heavy metals have been employed [Patterson, 1985]. Several alternative treatments have also been suggested in the literature for treating plating rinse wastewater. These include evaporation, reverse osmosis, electrodialysis, and activated carbon adsorption. Reviews of these have been presented [Watson, 1987; Muthukumran et al., 1995; Kim et al., 1999]. However, the current process for treating plating wastewater has a disadvantage because its complex steps may cause economic problems. Another important problem of plating wastewater treatment is the production of sludge with high water and heavy metals contents, which requires extra treatment such as precipitation and flocculation. Recently, some plating industries adopted heavy metal adsorption technology using ion exchange resin. But ion exchange resin has no selectivity to the alkaline metals and it is rather expensive. However, the biosorption process has advantages compared to other processes which include cheap cost of materials, ease of operation and selectivity over the alkaline metals [Pradhan et al., 1998; Lee et al., 2000]. Especially, several chemical modification methods have been tried for the purpose of increasing the adsorption capacity of Organic/Inorganic sorbent [Park et al., 1999; Kim et al., 1999, 2000; Lee et al., 1999]. Among them, carboxylated alginic acid showed high adsorption capacity for heavy metals of 5-6 meq/g dry mass. For application to the actual plating wastewater, the biosorbent was immobilized by PVA-Boric acid method [Jeon et al., 1998]. The object of this study is to apply to the plating wastewater for water reuse, and heavy and precious metal recovery using carboxylated alginic acid bead.

MATERIALS AND METHODS

The alginic acid used in this study was purchased from Sigma-Aldrich (U.S.A.). The reaction procedure for chemical modification of alginic acid was as follows. 5 g of alginic acid was oxidized in 10 mM solution of potassium permanganate at 30 °C for 30 min. Reacted mixture was separated by centrifugation and washed five times thoroughly with distilled water. After being dried at 60 °C, it was immobilized. The immobilization method has been presented in the literature [Jeon et al., 1998]. All sorption experiments were performed by using immobilized carboxylated alginic acid. Wastewater was obtained from the Panwall plating factory in Ansan, Korea and kept at room temperature before use. Generally, wastewater in the Panwall plating factory is re-collected in three types. This wastewater is divided as acid-alkaline wastewater, chelating wastewater, and chromic wastewater. The pH control and oxidation reaction were used as pretreatment methods for effectively removing heavy metals. Sodium hypochlorite, which is known as a strong oxidation reagent, was purchased from Aldrich Chemical Company, Inc. The procedure for all the biosorption experiment in batch was as follows. At first, sodium hypochlorite of 10 mM was reacted with wastewater for 1 hr at room temperature. Predetermined carboxylated alginic acid beads were put into a given amount of oxidized wastewater, and then mixed by shaking at 200 rpm in an incubator at 30 °C. The pH was adjusted periodically to pH 4.0 by adding 1 N NH_4OH and HNO_3 as required. When the pH of metal solution was maintained as 4.0, the solution was centrifuged at 11,000 G force for 20 min to remove suspending biosorbent, then metal concentration of the supernatant was analyzed by using AAS (Atomic Absorption spectroscopy: Perkin-Elmer 3110, USA) or ICP (Inductively Coupled plasma Spectroscopy: Perkin-Elmer ICPS-7500, UK). The COD was measured by using COD bottle and kit of HACH (German). The hardness was analyzed by using Wet method, and TOC (Total Organic Carbon) was measured with a TOC analyzer (Dohrman DC-80) by both combustion and UV-persulfate methods, which was calculated as the difference between the TC and the TIC values. The concentration of CN^- was measured by using Ion Chromatography. The reusability for carboxylated alginic acid beads and IR-

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120 plus resin was also investigated in batch operation. The metal-adsorbed adsorbent was washed, dried and then added to a flask containing 100 ml EDTA solution. The flask was shaken for 3 hours at 30 °C. Following desorption, the slurry was filtered and the metal concentration of the filtrate determined. The metal-desorbed adsorbent was used in the next cycle of adsorption and desorption. The above procedure was employed for five consecutive cycles.

Also, sequential operation experiments using packed-bed contact, which is a borosilicate glass column (I.D. 2.5*24 cm, bed volume=118 ml, Luer-Lock made by Sigma Chemical Co.), were performed. Flow rate was varied by using a Masterflex peristaltic pump and the concentrations of metal ions in influent and effluent were measured by AAS or ICP. Flow direction was up-flow in most column operations. Influent pH of wastewater was controlled to be 4.0 by using 1 N HNO_3 and NH_4OH. Prior to applying sequential operation, an oxidation reaction between sodium hypochlorite and chelating wastewater was made to occur for 1 hr. The pretreatment method for all sample to exclude inhibition of non-reacted organic materials followed 'Standard method' [Franson, 1989].

RESULTS AND DISCUSSION

To remove heavy metals in wastewater efficiently, various ion components in wastewater were analyzed. As shown in Table 1, copper and nickel ions were the main components in acid-alkaline wastewater. Also, most of the metal ions in chelating and chromic wastewater were nickel and chromic ion, respectively. In order to remove the metal efficiently, pretreatment was conducted.

1. Treatment for Chelating Wastewater

An adsorption capacity of carboxylated alginic acid beads was investigated without pretreatment of chelating wastewater. However, adsorption capacity of nickel ion was very low as 6.7 mg/g dry mass. It was known that various metal complexes, which are not removed by alkaline precipitation, had decreased adsorption capacity. The conventional processes in most chelating wastewater treatment contain oxidation reaction of wastewater using chelating agent [Joseph, 1995]. And oxidized wastewater was treated through coagulation and precipitation processes. So, oxidation process using sodium hypochlorite, which is known to be a strong oxidizing agent in pretreatment, was employed in this study. This oxidant plays an important role in breaking metal-ligand complexes and makes free ligand metal. During the oxidation reaction of sodium hypochlorite, chloride ion (Cl^-) may be produced. However, maximum concentration of chloride ion in oxidized wastewater is very low as 0.747 mg/*l*. This value was calculated from the 10 mM NaOCl used in this study. In particular, this value is much lower than that of the regulatory value (150 mg/*l*) for standard drinking water.

Table 1. Components of plating wastewater in Panwall plating factory (Unit: ppm)

	Acid-alkaline wastewater	Chelating wastewater	Chromic wastewater
Cu^{2+}	90.00	1.89	80.00
Zn^{2+}	2.00	1.34	0.34
Ni^{2+}	140.00	110.00	115.00
Cr^{3+}	11.76	2.72	200.00
TOC	134.47	240.54	23.84
CN^-	N.D	N.D	N.D
COD	70.00	192.00	176.00
SS	26.40	33.85	2.00
Hardness	35.46	33.17	18.28

*N.D: Not Detected

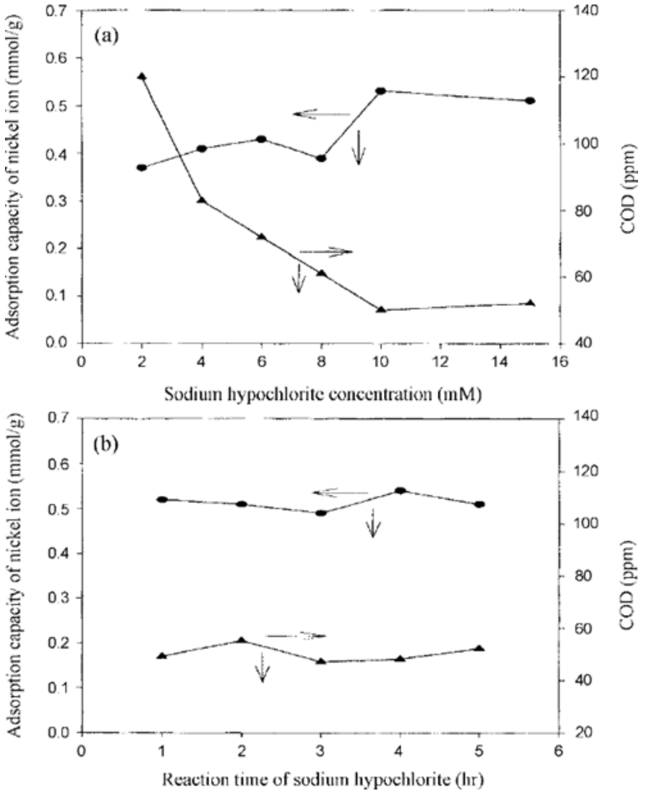

Fig. 1. The effect of concentration and reaction time of sodium hypochlorite on nickel adsorption capacity and COD in the chelating wastewater (Initial concentration of nickel ion and COD are 110 and 192 mg/*l*, respectively. Final pH: 4).
(a) The effect of sodium hypochlorite concentration. (b) The effect of reaction time between sodium hypochlorite (10 mM) and chelating wastewater

The effect of sodium hypochlorite on nickel adsorption capacity and COD change was investigated. As shown in Fig. 1(a), adsorption capacity of nickel ion was increased to about 25 mg/g dry mass in comparison to that without pretreatment. The adsorption capacity of carboxylated alginic acid beads was increased as the concentration of oxidant was increased. However, adsorption capacity of carboxylated alginic acid beads was almost the same in the range of over 10 mM concentration of sodium hypochlorite. The COD was about 45 ppm at the 10 mM concentration of sodium hypochlorite. This value means that sodium hypochlorite can decrease the COD about 74%. As expected, the adsorption capacity for heavy metal increased as the COD decreased. This can be explained as the increase of free metal resulting from decreasing COD amount through the oxidation reaction of metal-ligand complex. From the result, optimal concentration of sodium hypochlorite was chosen as 10 mM.

In general, it is also very important to decide reaction time for

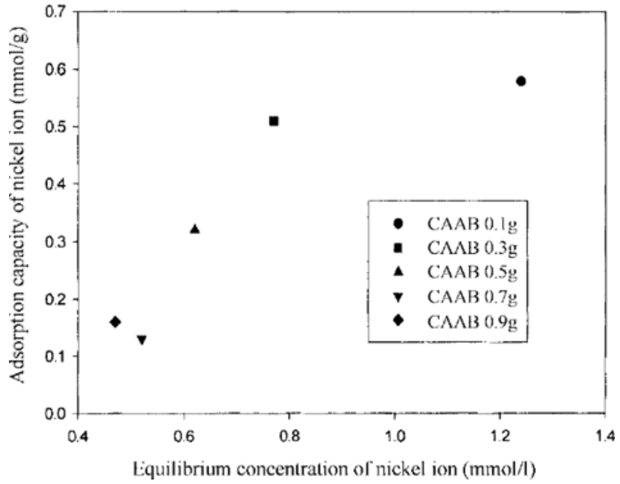

Fig. 2. Equilibrium concentration and adsorption capacity of nickel ion by the variation of weight of carboxylated alginic acid bead in the chelating wastewater (Total solution volume: 100 ml, Final pH: 4).

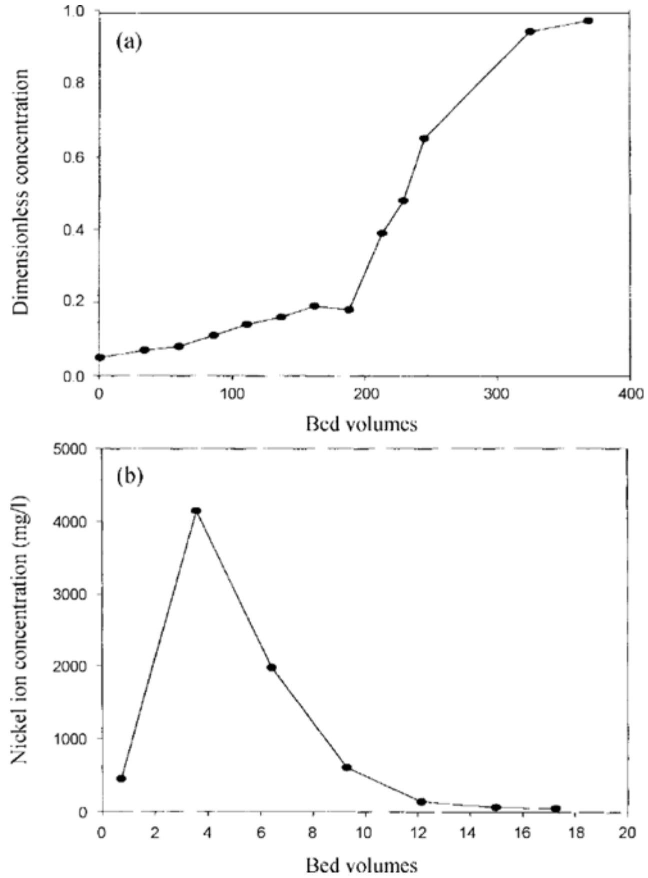

Fig. 3. Breakthrough curve of nickel ion using carboxylated alginic acid bead in the chelating wastewater and desorption using EDTA (Initial concentration of nickel ion: 110 mg/l, One bed volume: 70 ml, Influent flow rate: 5 ml/min).
(a) Breakthrough curve of nickel ion using carboxylated alginic acid bead. (b) Desorption of nickel ion from carboxylated alginic acid bead using EDTA

oxidation of wastewater. The results on nickel adsorption capacity and COD change for the reaction time between sodium hypochlorite (10 mM) and chelating wastewater are shown in Fig. 1(b). Since adsorption capacity of nickel ion and COD was not greatly affected by the reaction time, 1 hr was chosen as the reaction time.

Fig. 2 shows the adsorption capacity and equilibrium concentration of nickel ion in changing the weight of biosorbent. As expected, the adsorption capacity decreased while the weight of biosorbent increased due to the relatively large portion of the biosorbent compared to the total treatment efficiency increased. Especially, when the biosorbent of 0.9 g was loaded in the wastewater, the removal efficiency, which is defined as ratio of equilibrium and initial concentration of nickel ion, reached about 80%.

Carboxylated alginic acid beads were packed in glass column. Since the beads did not swell and have enough strength to sustain their weight (data not shown), channeling of flow and the increase of pressure drop were not observed in the column operation. The level of metal ions was expressed as ratio of influent metal concentration to effluent metal concentration. Fig. 3(a) shows the breakthrough curve of a column packed with carboxylated alginic acid beads when oxidized wastewater of 110 ppm at pH 4 was used as an influent. The dimensionless concentration of breakthrough point was set as 0.2. As shown in Fig. 3(a), the breakthrough point emerged around 200 bed volumes. This result means that the removal of 80% for nickel was possible within 200 bed volumes.

Nickel ions bound to immobilized carboxylated alginic acid was readily reversed by using EDTA which was known to be a very

Table 2. Adsorption capacity of carboxylated alginic acid bead in acid-alkaline and chromic wastewater

	Metals	Initial concentration (mg/l)	Final concentration (mg/l)	Adsorption capacity (mg/g)	Final pH
Acid-alkaline wastewater	Cu^{2+}	90	85.2	4.6	1.65
			50.5	38	3.99
	Ni^{2+}	140	135.9	3	1.65
			113.7	22	3.99
Chromic wastewater	Cr^{3+}	200	187.3	12	2.17
			145.1	52	4.03
	Cu^{2+}	80	70.9	7.2	2.17
			57.3	20	4.03
	Ni^{2+}	115	112.1	2.7	2.17
			105.2	7	4.03

strong desorbent for many heavy metals [Dawson et al., 1986]. Optimal concentration of EDTA was chosen as 0.01 N (data not shown). As shown in Fig. 3(b), nickel ions were readily desorbed from the column in just a few bed volumes. Also, a high concentration of nickel ions (about 4,150 mg/*l*) was recovered around 2-3 bed volumes. This value was corresponding to the 64 in terms of maximum concentration factor, which is defined as ratio of effluent and influent Ni^{2+} concentration.

2. Treatment for Acid-Alkaline Wastewater and Chromic Wastewater

The adsorption capacity of a carboxylated alginic acid bead for each wastewater without any pre-treatment was very low, as expected, because of low pH of the solution. The results are shown in Table 2. It was known that the adsorption capacity for heavy metals increased as the solution pH was increased [Volesky, 1990]. In order to increase the low adsorption capacity of carboxylated alginic acid bead, pH manipulation using NH_4OH and HNO_3 was adopted as a pretreatment method. As shown in Table 2 after pH control, the adsorption capacities of heavy metals in each wastewater greatly increased. In order to remove the effect of heavy metal removal by precipitation, final pH of the solution was manipulated as 4. In the case of acid-alkaline wastewater, adsorption capacity of copper ion was higher than that of nickel ion. This result can be thought of as the high selectivity to copper of carboxylated alginic acid bead. And, in the case of chromic wastewater, adsorption capacity of chromium (3+) was the highest. It is generally known that the selectivity of trivalent metal ion is higher than that of divalent metal ion for biosorbent [Kratochvil et al., 1998].

It is very important for a batch process to determine the optimal loading amount of the adsorbent so as to remove heavy metals under effluent regulatory concentration. As shown in Fig. 4, when 0.9 g of immobilized carboxylated alginic acid was loaded, removal efficiencies calculated from the ratio of equilibrium and initial concentration of copper and nickel ion in acid-alkaline wastewater were about 80% and 40%, respectively. And adsorption capacities for the two metal ions were decreased as the loading amount of the carboxylated alginic acid bead was increased.

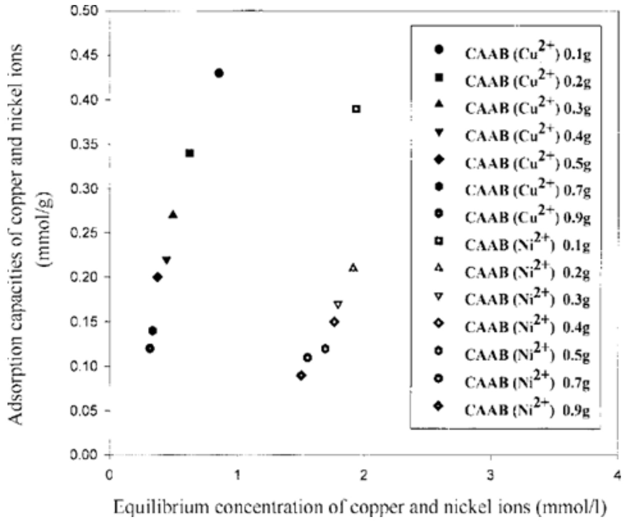

Fig. 4. Equilibrium concentrations and adsorption capacities of heavy metal ions by the variation of weight of the carboxylated alginic acid bead in the acid-alkaline wastewater (Total solution volume: 100 ml, Final pH: 4, Initial concentration of copper and nickel ion is 90 and 140 mg/*l*, respectively).

Sequential adsorption processes using glass column packed with immobilized carboxylated alginic bead were performed. Acid-alkaline wastewater controlled as pH 4 flowed into the column. All experimental conditions were the same with that of chelating wastewater treatment except the influent concentration. As shown in Fig. 5(a), while the breakthrough point of copper ion appeared around 350 bed volumes, that of nickel ion emerged at around 80 bed volumes. This result reflects that there exists a difference in affinity for carboxylated alginic acid bead between copper and nickel ion. Likewise for chelating wastewater, this result also shows the possibility for reuse as industrial water of the effluent.

Fig. 5(b) shows that copper and nickel ions were readily desorbed from the column in just a few bed volumes. The result also shows that desorption rate was much faster than that of adsorption rate. Also, thickness of high concentration for copper (4,300 mg/*l*) and nickel ion (2,800 mg/*l*) around 3-4 bed volumes was obtained, respectively.

3. The Comparison with Adsorption Capacity of Ion Ex-

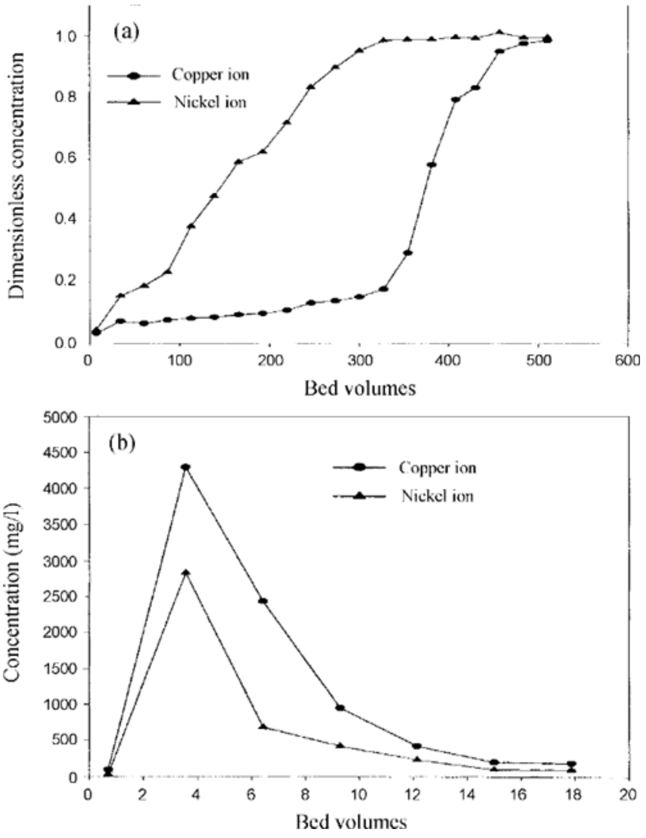

Fig. 5. Breakthrough curve of copper and nickel ions using carboxylated alginic acid bead in the acid-alkaline wastewater and desorption using EDTA (Initial concentrations of copper and nickel ion are 90 and 140 mg/*l*, respectively. One bed volume: 70 m*l*, Influent flow rate: 5 ml/min).

(a) Breakthrough curve of copper and nickel ions using carboxylated alginic acid bead. (b) Desorption of copper and nickel ions from carboxylated alginic acid bead using EDTA

Table 3. The comparison of adsorption capacity between carboxylated alginic acid bead and ion exchange resin (IR-120 plus resin) (Final pH: 4, Temperature: 30 °C) (Unit: mmol/g)

	Cu^{2+}		Ni^{2+}		Cr^{3+}	
	Acid-alkaline wastewater	Synthetic wastewater	Chelating wastewater	Synthetic wastewater	Chromic wastewater	Synthetic wastewater
Carboxylated alginic acid bead	0.55	0.87	0.52	0.70	1.52	1.78
IR-120 plus resin	0.21	-	0.17	-	1.35	-

change Resin (IR-120 Plus)

To test the capability of carboxylated alginic acid bead in real plating wastewater, a comparison of adsorption capacity at each wastewater between carboxylated alginic acid bead and ion exchanger IR-120 plus resin was performed. IR-120 plus resin is one of the commercial ion-exchange resins that has an adsorption capacity of 1-4 mmol/g dry mass [Bolto et al., 1988]. And the synthetic wastewater, whose concentrations of heavy metals were same as in the real wastewater but other components were not included for removing other effects on the adsorption capacity of heavy metals, were made for the blank test. The results are shown in Table 3. Adsorption capacities for heavy metals in real plating wastewater were lower than that in synthetic wastewater. This result implied that heavy metal adsorption was interfered with by various organic materials in most real plating wastewater. And it showed the superiority of carboxylated alginic acid bead compared to the IR-120 plus resin for most kinds of heavy metals in the wastewater.

In order to prove the superiority of the immobilized bead, the reusability for carboxylated alginic acid bead and IR-120 plus resin was investigated in batch operation. The results are shown in Table 4. The uptake capacities for two adsorbents were relatively maintained through cycles 1-5. It was also known that the cost of biosorbent was lower than that of commercial ion exchange resin [Chen et al., 1996]. Therefore, it is expected that the conventional plating wastewater treatment process using ion-exchange resin can be sufficiently replaced with economical processes using carboxylated alginic acid bead.

CONCLUSIONS

The carboxylated alginic acid immobilized with polyvinyl alcohol was used to reuse water and to recover heavy metals efficiently in the Panwall-plating complex wastewater, which is classified as acid-alkaline, chelating, and chromic wastewater. Since the bead did not swell and has enough strength to sustain its weight, channeling of flow and the increase of pressure drop were not observed through the column operation. To remove heavy metals efficiently, pre-treatment methods such as pH manipulation and oxidation reaction between sodium hypochlorite and wastewater was applied.

In the case of treatment of chelating wastewater, the removal of 80% for influent concentration of nickel ion was possible within the 200 bed volumes by using oxidation reaction in sequential operation. And, adsorbed nickel ions were readily desorbed from the column by using EDTA. Furthermore, a high concentration of nickel ions was recovered at around 2-3 bed volumes. For the treatment of acid-alkaline and chromic wastewater, the pH control of each wastewater was used as pre-treatment method. In the column working process, bed volumes for copper and nickel ions were about 350 and 80, respectively. These results reflect the difference of affinity for carboxylated alginic acid bead between copper and nickel ion. The removal efficiency of chromium (3+) was increased to about 21% in chromic wastewater in the batch process. These results show the possibility for reuse as industrial water and ease in recovering heavy metals of the effluent.

Finally, it also showed the superiority of carboxylated alginic acid beads compared to the IR-120 plus resin for most kinds of heavy metals in the wastewater. Consequently, it is expected that the conventional plating wastewater treatment process using ion-exchange resin can be sufficiently replaced with an economical process using carboxylated alginic acid beads.

Table 4. Reusability of carboxylated alginic acid bead and IR-120 plus resin on metal ions in plating wastewater (Final pH: 4, Temperature: 30 °C) (Unit: mmol/g)

Cycle number	Carboxylated alginic acid bead			IR-120 plus resin		
	Cu^{2+}	Ni^{2+}	Cr^{3+}	Cu^{2+}	Ni^{2+}	Cr^{3+}
1	0.55	0.52	1.52	0.21	0.17	1.35
2	0.48	0.45	1.38	0.21	0.18	1.37
3	0.43	0.42	1.35	0.20	0.17	1.34
4	0.46	0.43	1.41	0.22	0.15	1.35
5	0.44	0.41	1.39	0.21	0.18	1.31

ACKNOWLEDGMENTS

This study was supported by a research fund provided by the Korea Institute of Industrial Technology, Republic of Korea.

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