EVALUATION OF TWO ALTERNATIVES EFFICIENTLY AND ECONOMICALLY TREATING ELECTROPLATING WASTEWATER

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Abstract: Currently used neutralizer and reduction and oxidation processes in treating electroplating wastewater were comparatively refitted with two different processes because treating electroplating wastewater containing cyanides and heavy metals needs more complicated processes and increased treatment cost. Process A was performed as oxidation of cyanide, reduction of Cr^{6} and neutralization-sedimentation finally being achieved. Process B was conducted as reduction of Cr^{6} , neutralization-sedimentation, oxidation of cyanide and neutralization-sedimentation finally being accomplished.

Hypochlorite could oxidize cyanides at the greatest degree by up to 0.1 mg/L at the dosage of 7,000 mg/L compared to those of hydrogen peroxide and oxygen. The proper dosing of hypochlorite to completely oxidize cyanides was 4,000 mg Cl over 400 mg CN. For reducing Cr^{6^+} , NaHSO₃ was used. Its optimal dosage was 2.5 $SO_3^{2^+}/Cr^{6^+}$ in process A, whereas it was ranged from 1.5 to 1.6 $SO_3^{2^-}/Cr^{6^+}$ in process B. The difference of optimal dosage reflects from the residual chlorine formed due to chlorine overdosed for oxidizing cyanides in process A.

Employing Mg(OH)₂+NaOH for pH adjustment could reduce sludge volume up to 50% compared to using Ca(OH)₂ showing 25 kg in process A. For process B, it was not differently obtained among three neutralizers. Regardless of type of alkaline reagents being used, their sludge quantities in the process B were much less produced compared to that of process A. However, it was required that two extra facilities should be introduced for neutralization-precipitation processes and HCN up-taker.

Key Words: Cyanide and heavy metals removal, Electroplating wastewater treatment

INTRODUCTION

In general, electroplating wastewater including cyanides, Cu, Ni, Cr, and Zn as well as chelating agent, surfactant and organic reductant can impair on water environment once they are carelessly disposed. Heavy metals can be readily taken up to human body through food-chain and accumulated, which causes chronic and acute

toxicity leading to biological metaformation and physiological mutation as well as lethal death.¹⁾ Cyanides have more adverse toxicity against fish rather than human body and microorganisms. It has been known that 0.02 mg CN/L can kill fish.²⁾ Less than 0.2 mg CN/L can not make adverse impact on human body of which bioaccumulation can be avoided. Less than 30 mg CN/L can be biologically degraded by microorganisms.^{2,3)} Nickel reacts with other cations and DNA while in production, use and treatment process. For higher concentration, it may cause mutation of DNA and dermatitis, nephritis, diz-

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ziness and dyspnoea.⁴⁾ Chronic exposition against Zn cause vomiting, dehyration, electrolyte unbalance, abdominal pain, nausea, dizziness and nephritis.⁵⁾ Cu needs to produce red blood cell, but over dosage of it more than 300 mg/kg adverse impacts on human body.⁶⁾

Metals contained in electroplating wastewater has been treated by sedimentation, ion exchange, electrolysis and reduced pressure evaporation, but electroplating industry has weak financial basis so that they can only employ sedimentation process among others. Currently, neutralization-sedimentation processes in electroplating wastewater treatment plant carelessly employ various alkaline reagents and coagulants to treat heavy metals i.e. Cr, Cu, Ni. Aldrich⁷⁾ has used varying ratio of FeSO₄ · 7H₂O and Na₂SO₃ to reduce amount of sludge produced from the electroplating wastewater treatment plant. Tayler and Qasim⁸⁾ investigated an economical way in reducing chromate wastewater in response to dissolved oxygen concentration and pH.

Cyanide has been generally occurred from degreasing and hardening processes showing a few mg/L to hundreds mg/L, which deteriorate removal efficiency of heavy metals due to formation of cyanide-metal complexes as cyanide is reacted as a ligand.⁹⁾ It has been eventually treated by alkaline chlorination in conjunction with peroxide, ozone, Fenton oxidation and electrolysis. 10,111 Among them, Fenton oxidation produces HCN at acidic pH condition. Employing peroxide can result in occurrence of ammonia, which in turn forms amine complexes that consequently needs breakpoint chlorination. In the meantime, electrolysis may cost exceedingly in constructing related plant and maintenance of which effluent quality is not stable. Alkaline chlorination may be thus acceptable such that cyanide can be oxidized by Cl2 or NaOCl and then converted into CNO, comparably less toxic, which consequently degraded into CO₂ and N₂. 10) Electroplating wastewater has been exposed various range of pH between 2 and 12.

This study was thus conducted to evaluate the most efficient electroplating wastewater treatment

protocol in terms of proper use of type of neutralization agent and effective arrangement of the related process.

MATERIALS AND METHODS

Synthetic wastewater was prepared in the laboratory whose concentration was referred to the concentration sometimes highly flowing into the electroplating wastewater treatment facility.

Table 1 Water quality parameters for the laboratory prepared wastewater in 10 L of distilled water at pH 3

Compounds	Concentration (mg/L)		
CN	400		
Cu ²⁺	200		
Cr ⁶⁺	200		
Zn ²⁺	200		
Ni ²⁺	200		

CuCN, K_2CrO_4 , $ZnSO_4 \cdot 7H_2O$ and $NiSO_4 \cdot 6H_2O$ were used for the preparation, which was adjusted at pH 3 using H_2SO_4 .

Jar tester was used for Cr^{6^+} reduction and cyanide oxidation at $25\pm0.5^{\circ}C$ as shown in Figure 1.

Experiment for process A was performed as oxidation of cyanide, reduction of Cr^{6^+} and neutralization-sedimentation finally being per

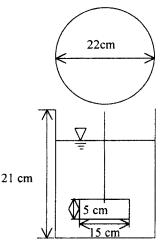


Figure 1. Schematic diagram of jar-tester used in this experiment.

formed. The oxidation of cyanide was conducted such that 6 L of the sample was each adjusted at pH 11 using nominal amount of NaOH, Ca(OH)2, Mg(OH)2+NaOH, respectively, following by addition of 4000 mg Cl/L using 12% (w/v) of NaOCl. After the reaction being completed, the solution was kept at pH 10.5 to 11 using NaOH and Ca(OH)2, which was then mixed at 200 rpm for 1 hr, thereafter 120 mL of sample was taken to determine residual concentration of cyanide and chlorine. Subsequently, the sample was adjusted at pH 3 using (1+1) H₂SO₄ thereof 120 mL of the sample was obtained to determine Cr6+ concentration, which was subsequently reduced by NaHSO3 at varying ratio of SO₃²-/Cr⁶⁺ at 200 rpm for 30 min. After that, residual chlorine and Cr6+ were observed. Consequently, the sample was each adjusted at pH 8.5 to 9.0 using nominal amount of NaOH, Ca(OH)₂, Mg(OH)₂+NaOH, respectively, and then mixed at 40 rpm for 20 min following by settling for 30 min. 120 mL of supernatant was taken to determine residual metal concentrations. After 24 hr, volume and weight of settled sludge was observed after it had been dried at 105°C for 24 hr.

Experiment for process B was conducted as reduction of Cr⁶⁺, neutralization-sedimentation, oxidation of cyanide and neutralization-sedimentation finally being accomplished. Cr6+ concentration in the sample at pH 3 was obtained, which was then reduced by NaHSO3 at varying ratio of SO₃²-/Cr⁶⁺ at 200 rpm for 30 min. After that, Cr⁶⁺ concentration and pH were obtained. The sample was each adjusted at pH 8.5 with nominal amount of NaOH, Ca(OH)2, Mg(OH)2 +NaOH, respectively, which was then mixed at 40 rpm for 20 min. Cyanide concentration was obtained after the sample had been settled down for 30 min. After 24 hr, settled sludge volume and weight were obtained after it had been dried at 105°C for 24 hr. The sample was then adjusted at pH 10.5 to 11.0 using NaOH and Ca(OH)2, which was then oxidized by 4,000 mg Cl/L using 12 (w/v) % of NaOCl at 200 rpm for 1 hr. After that, residual cyanide and chlorine concentration were obtained. It was then adjusted at pH 7 using (1+1) H₂SO₄, which was mixed with 5 mg/L of SA-307 (Anionic polymer, Songwon) at 40 rpm for 20 min. Residual metal concentration was obtained after the sample had been settled down for 30 min. After 24 hr, settled sludge volume and weight were observed after it had been dried at 105°C for 24 hr.

Process B may produce HCN in a reduction process of Cr⁶⁺ such that captured HCN was then returned into the oxidation process of which cyanide concentration was re-adjusted at 400 mg/L. For experiment of process A, coagulation process was conducted by only pH adjustment, but for experiment B, 5 mg/L of SA-307 was used because suspended particles in micro-size were observed due to presence of residual chlorine. Figure 2 and 3 represent schematic diagram of experiments for processes A and B, respectively.

Concentrations of CN⁻ and Cr⁶⁺ were observed in accordance with Standard Methods. ¹²⁾ Cr³⁺, Cu²⁺, Zn²⁺ and Ni²⁺ concentrations were quantified by Inductively Coupled Plasma (SPQ 9000, Waters) after the sample had been digested by nitric acid. ¹²⁾ The concentration of Cr³⁺ was obtained since amount of digested Cr⁶⁺ has been

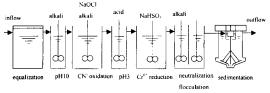


Figure 2. Schematic diagram of process A in treating electroplating wastewater.

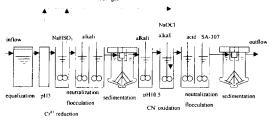


Figure 3. Schematic diagram of process B in treating electroplating wastewater.

subtracted from sum of digested and non-digested Cr^{6^+} . Prior to summation of Cr^{6^+} , concentration of non-digested Cr^{6^+} had been previously quantified. NH^{4^+} -N concentration was determined by Ion Analyzer (EA-920, Orion). Turbidity was obtained by turbidity meter (Tr-701). pH was observed by pH meter (370A, Orion).

RESULTS AND DISCUSSION

Cyanide Oxidation

400 mg/L of cyanide was oxidized by H_2O_2 whose concentration was increased up to 3:1 of molar ratio of H_2O_2/CN as shown in Figure 4. It was lowered to 139 mg/L at 3:1 of H_2O_2/CN . In response, NH_4^+ -N concentration increased up to 3 mg/L. It demonstrated that cyanide could be transformed into ammonium ion as described in Equation (1) and (2).

$$CN^{\circ} + H_2O_2 \rightarrow CNO^{\circ} + H_2O \tag{1}$$

$$CNO^{2} + 2H_{2}O_{2} \rightarrow NH_{4}^{3} + CO_{3}^{2}$$
 (2)

At 0.5 of H_2O_2/CN , which equivalent to 242.86 mg/L of H_2O_2 added, amount of cyanide theoretically removed was expected to be 185.72 mg CN^*/L . However, cyanide practically removed was 214.28 mg CN^*/L , which simply indicated that 28.56 mg CN^*/L of HCN could be stripped off from the jar during the experiment.

A total of molar ratio of 5 employing either NaOC1 or H_2O_2 over CN was introduced to oxidize cyanide as shown in Figure 5. Dosing greater H_2O_2 or less NaOC1 could not improve

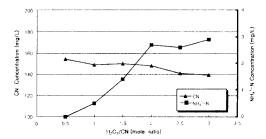


Figure 4. Cyanide oxidation on increasing molar ratio of H_2O_2/CN at pH 9(\pm 0.5).

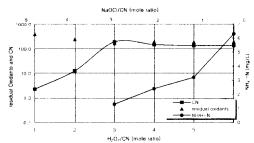


Figure 5. Cyanide oxidation on varying moral ratio of NaOCl/CN or H₂O₂/CN at pH 9.0(±0.5).

the extent of cyanide removal efficiency while residual NH₄⁺ concentration increased.

However, for greater molar ratio of 4 to 5 of NaOCI/CN, cyanide removed while residual NH₄⁺ was never observed. Reducing molar ratio of NaOCI/CN to less than 3 initiated generation of NH₄⁺ as oxygen radical released from H₂O₂ began engaging in producing NH₄⁺ as a byproduct. For that reason, H₂O₂ may not be preferably used for reagent in efficiently oxidizing cyanide. At higher pH of 10.5(±0.5), cyanide was oxidized on varying concentration of NaOCI ranging from 1,500 to 7,000 mg/L. Adding more than 4,000 mg/L of NaOCI satisfactorily could meet with regulation standard showing less than 1 mg CN/L.

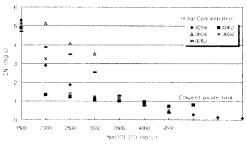


Figure 6. Cyanide oxidation according to the addition of NaOCl.

Cr⁶⁺ Reduction

200 mg/L of Cr⁶⁺ and 400 mg/L of cyanide was once prepared at pH 3 in process A, which was each neutralized to pH 7 by employing NaOH, Ca(OH)₂ and Mg(OH)₂+NaOH while 4,000 mg/L of NaOCI was applied for oxidizing cyanide. In response, residual Cr⁶⁺ concentration

was observed at 183, 163, and 113 mg/L, whereas residual chlorine concentration was obtained at 760, 613, and 163 mg/L, respectively. To further reduce Cr^{6+} , NaHSO₃ was applied based on molar ratio over Cr^{6+} concentration ranging from 1.5 to 3.0 as shown in Figure 7 and 8.

Employing NaOH could reduce Cr⁶⁺ at a greatest extent showing less than 1 mg/L for molar ratio of 2 of NaHSO₃/Cr⁶⁺, while two other cases still exposed higher concentration of Cr⁶⁺ showing more than 15 mg/L. Likewise, residual chlorine contacting with NaOH was at the lowest revealed less than 0.1 mg/L for molar ratio of 3 of NaHSO₃/Cr⁶⁺.

100 mg/L of Cr⁶⁺ was prepared at pH 3 in process B, which was in turn reduced by varying concentration of NaHSO₃ as shown in Figure 9. Cr⁶⁺ could be completely reduced by adding 350 mg/L of NaHSO₃, which was consumed greater amount than that of theoretically demanded showing 302 mg/L.

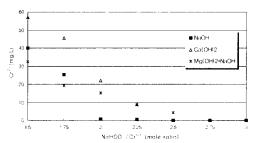


Figure 7. Cr⁶⁺ reduction using NaHSO₃ after pH being adjusted by NaOH, Ca (OH)₂, Mg (OH)₂+NaOH, respectively, in process A.

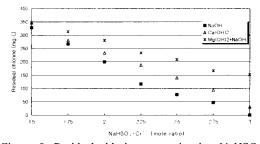


Figure 8. Residual chlorine removal using NaHSO₃ after pH was adjusted by NaOH, Ca (OH)₂, Mg(OH)₂+NaOH, respectively, in process A.

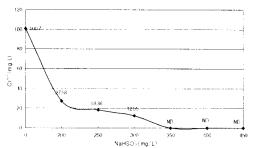


Figure 9. Cr⁶⁺ reduction in accordance with Na HSO₃ being added in process B.

Removal of Metal Compounds

Metals such as Cr, Cu, Zn and Ni were removed as metal hydroxides using NaOH, Ca(OH)₂ and Mg(OH)₂+NaOH were each used in process A as shown in Figure 10 to 12, respectively. It can obtain optimal pH to efficiently remove metal compounds at the lowest degree. All of three neutralization conditions could successfully meet with regulation standards for each compound (i.e., Cr : 2 mg/L, Cu : 3 mg/L, Zn: 5 mg/L, Ni: ND) at more than pH 8.5 except for Ni. Employing NaOH can decrease Ni concentration as low as 0.03 mg/L at pH 10 while it was still exposed at higher concentration of 0.25 and 0.5 mg/L at pH 10 by adding Ca(OH)₂ and Mg(OH)₂+NaOH, respectively. For NaOH, metals concentration showed less than 1 mg/L at pH 9 to 10 while for Ca(OH)₂ they was revealed at the lowest concentration at pH 9, but increasing pH more than pH 9 attributed to slight increase of metal concentration due to settling property being worsened. For Mg(OH)2 +NaOH, the extent of metals being reduced was comparatively dependent upon pH. For Ni, residual concentration has been decreased as pH was increased, but for Cu, Cr and Zn, their residual concentrations were rather slightly increased at more than pH 8. Nevertheless, pH 9 can obtain acceptable level of effluent water quality for metal compounds. It was well consistent with the result observed by Lanotte¹³⁾ who has found that using NaOH can reduce metals such as Cr, Cu, Zn and Ni at the lowest degree at pH 9.5, while Ca(OH)₂ can decrease them at the lowest extent at pH 8.5.

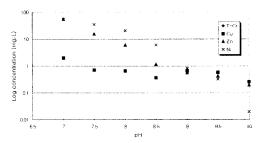


Figure 10. Variation of residual soluble metal concentration on pH being increased by NaOH in Process A.

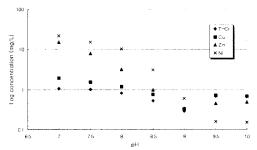


Figure 11. Variation of residual soluble metal concentration on pH being increased by Ca(OH)₂ in process A.

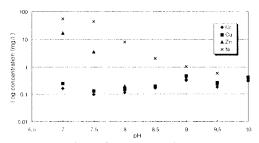


Fig. 12 Variation of residual soluble metal concentration on pH being increased by Mg(OH)₂+NaOH in process A.

In the following, metal compounds (i.e. Cr, Cu, Zn and Ni) were removed by employing each of NaOH, Ca(OH)₂ and Mg(OH)₂+NaOH, respectively, after Cr⁶⁺ had been reduced by NaHSO₃ in process B as shown in Figure 13. Adding NaOH could remove Cr at the greatest extent showing 0.35 mg/L at pH 8.5. Employing Mg(OH)₂+NaOH showed the highest residual concentration among others even though it could be reduced as low as 1 mg/L at pH 8 to 8.5. Unlike, level of residual Cu and Ni was relatively high presented due to complex formed

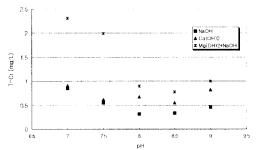


Figure 13. Residual chromium concentration after NaOH, Ca(OH)₂ and Mg(OH)₂ and NaOH were each used for neutralization and first sedimentation in Process B.

with residual cyanide. However, it will be expected to be further removed after cyanide complex will be oxidized.

After cyanide complexes contained in the effluent from the primary sedimentation being treated with 4,000 mg/L of NaOCl, residual metals were treated by NaOH, Ca(OH)2 and Mg(OH)₂+NaOH as shown in Figure 14, 15, and 16, respectively. As observed previously, Cu was still at higher degree present at approximately 1 mg/L among others, which will be needed to be removed further in secondary sedimentation. Employing NaOH (Figure 14) could meet with regulation standards of Cu (i.e. 3 mg/L) and Ni (i.e. ND) at more than pH 8. At pH 9, the lowest concentrations of them were observed at less than 1 mg/L. Employing Ca(OH)₂ generally exposed lower residual concentration of metals among others, thereby regulation standards of them were satisfactorily met with at more than pH 7. At pH 9.5, the lowest residual concentration of metals was observed at less than 0.5 mg/L. Mg(OH)₂+NaOH showed the similar level of residual concentration as NaOH solely being applied. Three conditions for neutralization gave all reliable metals concentration in effluent at more than pH 8.5. However, darkish colored oxidized micro-particles were occurred from cyanide oxidation due to reaction with residual chlorine, which were eventually suspended like colloidal particles, which in turn could deteriorate settling property resulting in approximately

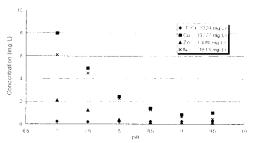


Figure 14. Residual soluble metal concentrations after NaOH being applied in final sedimentation of Process B.

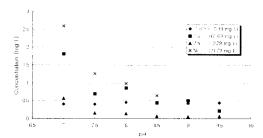


Figure 15. Residual soluble metal concentrations after Ca(OH)₂ being applied in final sedimentation of Process B.

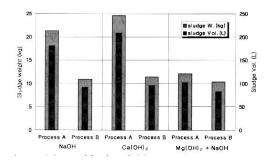


Figure 16. Residual soluble metal concentrations after Mg(OH)₂ and NaOH being applied in final sedimentation of Process B.

30 mg/L of residual turbidity. It was thus further treated by 5 mg/L of SA-307 so that residual turbidity was lowered to less than 1 mg/L, but it was still much more turbid than that observed from the process A.

Comparison of sludge production and management cost between two processes

Volume and weight of sludge were compared with regard to type of neutralizer and process employed (Figure 17).

For process A, employing Mg(OH)₂+NaOH

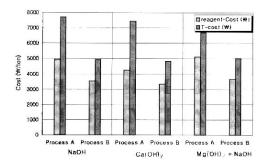


Figure 17. Comparison of sludge volume and weight between process A and B.

could reduce volume of sludge at the highest extent by 50% among others, while employing Ca(OH)₂ obtained the greatest amount of sludge volume showing 215 L. Likewise, weight of sludge employing Mg(OH)₂+NaOH exposed the lowest value, while employing Ca(OH)₂ revealed the greatest amount of sludge weight showing 21.6 kg. For process B, production of volume and weight of sludge were not significantly varied dependent upon type of neutralizer. Regardless of type of chemicals being varied, process B generally produced lower amount of sludge compared to that of the process A.

In response, moisture content was determined as given in Table 2.

For process A, the lowest moisture content of sludge was observed from dosing Mg(OH)₂+ NaOH, while it was obtained from dosing Ca(OH)₂ in process B.

Table 3 presents the comparison of sludge handling cost between process A and B.

For process A, using Ca(OH)₂ was needed to pay for the lowest chemical cost, whereas employing Mg(OH)₂ showed the lowest sludge handling cost. Total sludge management cost was presented at the lower rank in the order as follows; Mg(OH)₂+NaOH<Ca(OH)₂<NaOH. In other words, employing Ca(OH)₂ could save the cost by up to 3.5% compared to that of NaOH.

Table 2 Comparison of moisture content (%) of the sludge between process A and B

	NaOH	Ca(OH) ₂	Mg(OH) ₂ +NaOH
Process A	80	85	72
Process B	85	76	80

between Process A and B								
		Wet sludge volume (L/m³)	weight	ucaunent	Chemical cost (\$/m³)	Total cost (\$/m³)		
Process A	NaOH	180	21	2.2	4.0	6.2		
	Ca(OH)2	208	25	2.6	3.4	6.0		
	Ma(OH) ₂ +NaoH	102	12	1.3	4.1	5.4		
	NaOH	92	11	1.1	2.8	3.9		
	Ca(OH)2	96	11	1.2	2.7	3.9		
	Mg(OH) ₂ +NaOH	88	10	1.0	2.9	3.9		

Table 3 Comparison of sludge management cost between Process A and B

Moreover, it could save much more by approximately 13% at using Mg(OH)₂+NaOH. For process B, the total cost was not differed from each other. From Figure 17 and Table 3, process B was more efficient and economical than that of process A because H₂SO₄ and alkaline chemical was not needed for reduction of Cr6+. In addition, metals were satisfactorily removed from the primary sedimentation such that smaller amount of neutralizer was consumed to reach agreeable pH, which in turn could reduce sludge production and sludge management cost. However, process B might be necessarily required that an additional set of neutralization/coagulation tank should be installed, which attributes to increase of construction and building cost. Aside from, it might be needed to introduce nominal concentration of anionic polymer (i.e., 5 mg/L of SA-307) as coagulant additive such that effluent may still contain higher extent of darkcolored residual turbidity and chlorine. If alkaline electroplating wastewater is entered into the process A of treatment plant, it may not need to use alkaline chemical to oxidize cyanide. It could help additionally save chemical and sludge management cost in process A, which could make it more preferable for economically treating electroplating wastewater than process B.

CONCLUSIONS

For cyanide oxidation, employing NaOCl satisfied to meet with regulation standard of

cyanide, while cyanide was not properly treated by either H₂O₂ or NaOCl and H₂O₂.

For process A, employing NaOH could reduce Cr⁶⁺ at a greatest extent showing less than 1 mg/L for molar ratio of 2 of NaHSO₃/Cr⁶⁺, whereas residual chlorine contacting with NaOH was at the lowest revealed less than 0.1 mg/L for molar ratio of 3 of NaHSO₃/Cr⁶⁺. For process B, Cr⁶⁺ could be completely reduced by adding 350 mg/L of NaHSO3. For process A, all of three neutralization conditions could successfully meet with regulation standards for each compound at more than pH 8.5 except for Ni²⁺. Nevertheless, employing NaOH can decrease Ni²⁺ concentration as low as 0.03 mg/L at pH 10. For process B, adding NaOH can remove Cr⁶⁺ at the greatest extent showing 0.35 mg/L at pH 8.5. Unlike, level of residual Cu²⁺ and Ni²⁺ was relatively highly presented due to complexes formed with residual cyanide.

Regardless of types of neutralization chemicals (i.e. NaOH, Ca(OH)2, Mg(OH)2+NaOH) being varied, process B produced lower degree of sludge compared to that of process A. For process A, employing Mg(OH)2+NaOH showed the lowest total cost due to cut-down of sludge management cost. In comparison, for process B, it was not differed from each other. Process A does not have HCN problem, but it needs more expensive chemical cost, and more increased sludge production. Nevertheless, sludge production and chemical cost can be saved if alkaline electroplating wastewater may be entered into process A of the treatment plant. Process B needs additional set of neutralization/coagulation and sedimentation tanks being installed and also HCN control system being required, which subsequently might need to increase initial investment cost for construction and building. Moreover, it is also needed to install additional facility to reduce relatively higher turbidity due to residual chlorine present after secondary sedimentation being implemented.

It is consequently decided that process A can be selected as more efficient and economic process where amount of NaOCl, NaHSO₃ and Mg(OH)₂+NaOH can be properly used for agreeable removal of cyanide and Cr⁶⁺ with lower amount of sludge produced in treating alkaline electroplating wastewater.

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