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Treatment of Metal Finishing Wastewater in Sequencing Batch Process

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ABSTRACT

Metal finishing wastewater contains heavy metals, acids, alkalis, detergents and toxic chemicals such as cyanide far above the Standard B limits of the Environmental Quality (Sewage and Industrial Effluent) Regulation 1979. A sequencing batch process utilising two-tank system was selected to treat such wastewater from a small metal finishing plant in Kuala Lumpur. Treatment with lime and ferrous sulphate complexed and precipitated the cyanide and reduced hexavalent to trivalent chromium which was then precipitated along with other metals as metal hydroxides. The pH of effluent was accordingly adjusted. The pilot plant was designed to run automatically according to a chosen treatment and schedule. The quality of wastewater treated as above was found to meet the Standard B limits.

ABSTRAK

Air buangan industri penyiap logam mengandungi logam berat, asid, alkali, detergen dan bahan kimia toksik seperti sianida pada kepekatan yang jauh melebihi had Piawaian B, Peraturan Kualiti Alam Sekitar (Kumbahan dan Efluen Industri) 1979. Proses sesekumpul berjujukan yang menggunakan sistem dua-tangki telah direkabentukkan untuk merawat air buangan tersebut yang diluahkan oleh sebuah kilang penyiap logam di Kuala Lumpur. Perawatan yang menggunakan kapur dan besi (II) sulfat mengkompleks dan memendakkan sianida dan menurunkan kromium heksavalen kepada trivalen. Semuanya kemudian dimendakkan bersama logam lain sebagai logam hidroksida. pH efluen kemudian dilaraskan mengikut keperluan. Loji rintis ini direkabentukkan untuk berfungsi secara automatik mengikut sesuatu perawatan dan jadual terpilih. Kualiti air buangan yang telah dirawat didapati memenuhi had Piawaian B.

KEYWORDS

Heavy metals, metal finishing, cyanide complexation, heavy metal precipitation, chromium reduction, sequencing batch process, toxic waste, electroplating wastewater.

INTRODUCTION

More than 57% of acidic and alkaline wastewater and sludges containing toxic heavy metals are generated by small and medium scale metal finishing industries [1]. Most of these industries do not comply with the Department of Environment (DOE) discharge standards and dump wastewater into public drains. The waste eventually reaches rivers and the sea or groundwater.

Among reasons given for non-compliance are financial constraints, limited land area within their premises and lack of technical know-how and skilled operators to operate the facilities. Discharged wastewater contains heavy metals, such as Cr^{6+}, Cr^{3+}, Ni, Cu, Zn, Sn, Fe, acids, alkalis, detergents and toxic chemicals such as cyanide. This metal finishing wastewater (MFWW) is extremely dangerous because of its toxicity and possible mutagenicity to humans and other living things.

The contents of the wastewater originate from the various operations in metal finishing processes. Acids and alkalis are used in cleaning baths, such as acidic stripping baths using sulphuric, hydrochloric and nitric acids and alkaline stripping baths as well as hydroxides, sulphides or cyanides. Oil and grease are removed by alkaline cleaners and organic solvents which are generally petroleum or coal tar emulsions. Alkaline cleaners contain phosphates, silicates, carbonates, hydroxides, wetting agents and emulsifiers. The volume of wastewater generated by each plant varies widely ranging from 0.9 m^3/day to 500 m^3/day depending on the amount of work done. The pH of most of MFWW surveyed falls outside the Standard B limit of the Environmental Quality (Sewage and Industrial Effluent) Regulation 1979, which is 5.5 - 9.0 [2]. Even plants with wastewater treatment have discharges with pH exceeding the Standard B limit. About 45% of the surveyed premises have suspended solids contents greater than the Standard B limit of 100 mg/L [2]. The wastewaters contain heavy metals, for example, the MFWW from one plant had 11 mg/L Cr^{6+}, 48 mg/L Cr^{3+}, 159 mg/L Ni, 85 mg/L Zn and 224 mg/L Fe. The concentration of heavy metals in MFWW may range up to greater than 1000 mg/L. Typical electroplating wastewater quality as compared to the Standard B is shown in Table 1.

MATERIALS AND METHODS

DESIGN OF TREATMENT PROCESS

Small and medium scale electroplating industries generally lack space and skilled or knowledgeable operators. It is thus necessary for the design of the treatment plant to be inexpensive, compact, of easily understood technology, simple to operate and yet reliable.

The cheapest electroplating wastewater treatment process of commercial standing at present is the chemico-physical treatment. The technology involved is easy to understand since the main part of the process is chemical precipitation followed by coagulation and settling. The unit processes incorporated in such treatment plant are:

1. Grease and oil removal.
2. Chemical precipitation (to remove cyanide, chromates and heavy metals).
3. Flocculation and settling.
4. Neutralisation.
5. Sludge handling.

TABLE 1. Typical wastewater characteristics from small and medium metal finishing plants

No.	Type of Plating	m^3 day^{-1}	pH	Concentration (mg/L) SS	Cd	Cr^{6+}	CN	Pb	Cr^{3+}	Cu	Ni	Sn	Zn	Fe
1.	Ni, Cr, Cu	27.8	7.5	1,840	nd	nd	nd	nd	nd	21.0	4.2	nd	0.9	2.9
2.	Ni, Cr, Zn, Brass	1.6	6.5	nd	nd	nd	23.0	nd	nd	nd	nd	nd	nd	nd
3.	Ni, Cr, Zn, Au, Brass	1.5	5.7	130	nd	nd	7.8	nd	0.1	nd	0.8	nd	6.5	nd
4.	Ni, Cr, Zn, Cd, Brass	3.7	5.9	160	nd	nd	43.0	1.1	nd	2.6	11.0	nd	34.0	21.0
5.	Ni, Cr, Cu	3	6.8	110	nd	3.7	nd	nd	3.7	1.2	0.3	nd	17.0	45.0
6.	Ni, Cr, Zn	48	7.1	nd	nd	nd	3.6	nd	nd	nd	nd	nd	nd	nd
7.	Ni, Cr, Zn	22.2	10.2	50	nd	nd	19.0	nd	nd	nd	3.8	nd	54.0	nd
8.	Ni, Cr, Zn	3.7	5.2	450	nd	nd	nd	nd	1.0	0.1	0.2	nd	54.0	nd
9.	Ni, Cr, Zn	4.1	8.5	3	nd	nd	nd	nd	nd	nd	0.1	nd	nd	nd
10.	Na, Cr, Zn	1.8	5.7	80	nd	11.0	nd	nd	0.2	1.9	159.0	nd	7.3	0.8
11.	Ni, Cr, Zn, Sn, Ag	3.5	3.1	120	nd	nd	7.8	nd	nd	0.7	1.8	nd	75.0	21.0
12.	Ni, Cr, Zn, Cu, Brass	0.9	6.4	nd	nd	nd	66.0	nd	nd	nd	nd	nd	nd	nd
13.	Ni, Cr, Zn, Sn, Ag	1.3	5.6	330	nd	nd	24.0	nd	nd	4.7	6.2	nd	18.0	nd
14.	Ni, Cr, Zn	4	5.9	50	nd	nd	nd	0.2	nd	nd	27.0	nd	0.4	7.8
15.	Ni, Cr	3.5	2.8	10	nd	nd	nd	nd	24.0	nd	57.0	nd	0.1	7.1
16.	Zn, Bringt, Tin	4.3	7.5	800	nd	nd	76.0	nd	nd	nd	nd	nd	85.0	12.0
17.	Ni, Cr, Cu	3.9	3.8	660	nd	nd	nd	0.2	28.0	224.0	0.3	nd	3.0	10.3
18.	Ni, Cr, Zn, Brass	11.2	6.6	10	nd	nd	20.0	nd	0.2	0.1	0.1	nd	1.3	nd
19.	Ni, Cr, Zn, Cu, Sn	1.5	6.2	670	nd	nd	nd	nd	4.2	0.3	0.1	nd	16.0	9.8
20.	Ni, Cr, Zn, Sn, Brass	3.1	9.6	24	nd	nd	24.0	0.1	0.1	nd	0.1	nd	0.2	0.7
21.	Ni, Cr, Zn	1.3	4.7	410	nd	5.4	46.0	0.2	48.0	0.4	20.0	nd	54.0	61.0
22.	Ni, Cr, Zn	2.3	2.2	140	nd	nd	20.0	nd	6.2	0.4	6.7	nd	6.1	224.0
Standard B EQ(SIE) R 1979		-	5.5-9.0	100	0.02	0.05	0.10	0.5	0.05	1.0	1.0	1.0	1.0	5.0

nd: non-detectable

The chemical precipitation processes involved the following:

1. Reduction of hexavalent chromium to its trivalent state, which is more readily precipitated.
2. Oxidation of cyanide to the less toxic cyanate.
3. Precipitation of heavy metals (including trivalent chromium) as metal hydroxides in alkaline conditions.
4. Otherwise, wastewater containing a mixture of hexavalent chromium and cyanide can be treated with lime and ferrous sulphate. Cyanide is precipitated by complexation and the hexavalent chromium reduced and precipitated as a metal hydroxide.

In order to treat typical mixed wastewater from small and medium-scale electroplating plants, processes (1), (2) and (3) above would require a minimum of three reaction tanks (Three-tank system). However, if process (4) is used, only two reaction tanks are required (Two-tank system). This system is thus prefered in this case as it is a simpler and cheaper and does not involve corrosive chemicals.

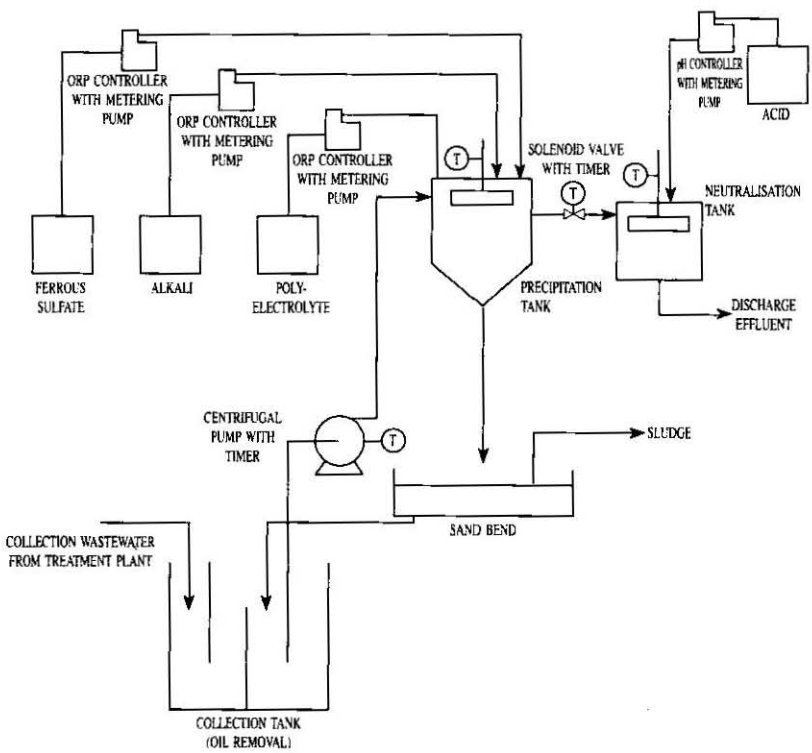


FIGURE 1. Process flowchart for wastewater treatment

A sequencing batch (SB) process has been selected for the design of a pilot plant. The process flow chart is shown in Figure 1. The pilot plant is capable of treating a wastewater flow of 20 L/hour. The sequence of operation is shown below:

Sequence of operation of batch pilot plant

Step 1: 20 L wastewater is pumped into the collection tank using a preset timer control. Any oil, grease or solids will be retained here.

Step 2: Wastewater is pumped into the precipitation tank using a preset timer control.

Step 3: Main treatment reactions - The pH and ORP are controlled by dosing sodium hydroxide and ferrous sulphate, respectively.

Step 4: Settling of precipitates after flocculation.

Step 5: The supernatant (20 L) is gravity-drained into the neutralisation tank by means of a timer-controlled solenoid valve.

Step 6: Neutralisation.

Step 7: Treated effluent is discharged.

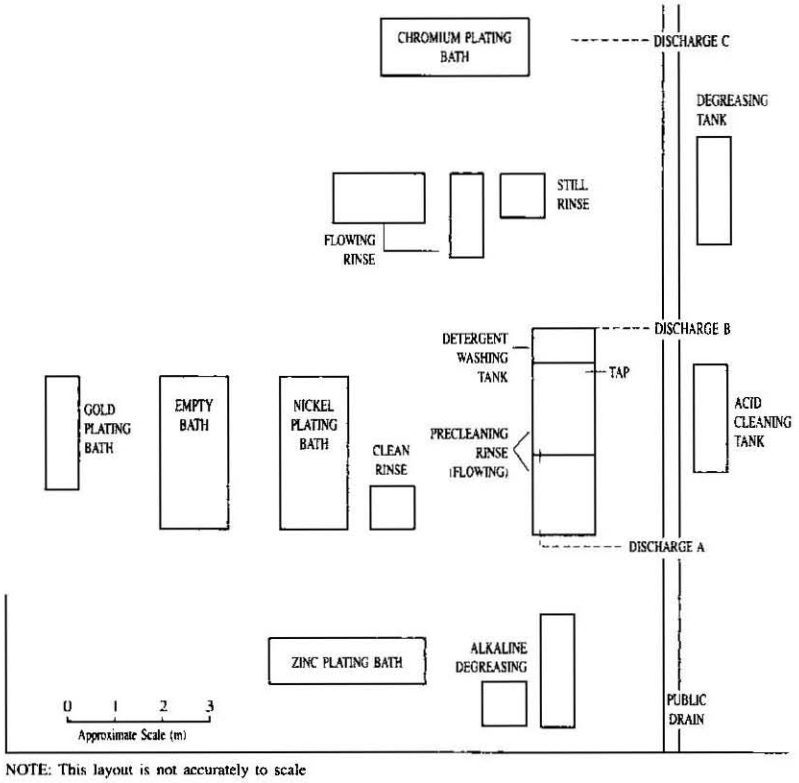
WASTEWATER SAMPLING AND ANALYSIS

Samples were obtained from a small metal finishing plant (Malaya Electroplating Sdn. Bhd., Sungai Besi, Kuala Lumpur). The plant carries out three main operations, namely welding and product forming, polishing and electroplating. The plating section generates wastewater containing heavy metals such as Cr, Ni and Zn and acids and alkalis containing cyanide.

Water samples from each of flowing rinse tanks, upstream, midline and downstream discharge points (Figure 2) were taken on five different days. All samples were taken at about 11.30 a.m, at which time, work in this factory has reached its fullest capacity.

The samples were analysed for chemical oxygen demand (COD), suspended solids (SS), chloride (Cl^-), sulphate (SO_4^{2-}), cyanide (CN^-), hexavalent and trivalent chromium (Cr^{6+} and Cr^{3+}) and heavy metals according to the standard methods [3]. The metals were analysed using flame Atomic Absorption Spectrophotometer (Perkin Elmer 1100 B).

For treatment using the SB process, wastewater was taken from the still rinse tank and diluted with wastewater from flowing rinse tanks so as to obtain a feed representative of wastewater from the plant. Samples were analysed prior to and after treatment.



NOTE: This layout is not accurately to scale

FIGURE 2. Existing plant layout at Malaya Electroplating Sdn. Bhd.

TREATMENT BY SEQUENCING BATCH PILOT PLANT

The demonstration plant as shown in Figure 3 was constructed at Malaya Electroplating Sdn. Bhd. The plant was designed to run automatically by the setting of timers according to a chosen treatment sequence and schedule. Once the construction was completed, the plant was commissioned and then operated at various conditions.

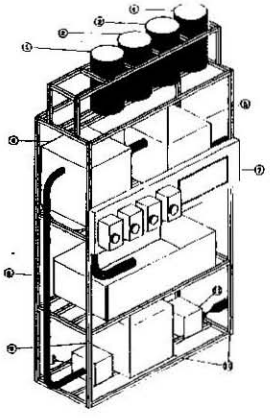


FIGURE 3. Wastewater treatment demonstration plant at Malaya Electroplating Sdn. Bhd.

Component No.	Description	Material
1.	Alkali feed tank to supply base into precipitation tank via pH controller	Epoxy-based G.R.P
2.	Ferrous sulphate feed tank to supply into precipitation tank via ORP controller	Epoxy-based G.R.P
3.	Polyelectrolyte feed tank to supply flocculant into precipitation tank via peristaltic metering pump (not shown).	Epoxy-based G.R.P
4.	Acid feed tank to supply acid into neutralisation tank via pH controller.	Epoxy-based G.R.P
5.	Neutralisation tank c/w stirrer (not shown)	Epoxy-based G.R.P
6.	Precipitation tank c/w stirrer (not shown)	
7.	Control panel consisting of:- - 2 pH controllers - 2 ORP controllers (including 1 spare unit) - 4 timers.	Epoxy-based G.R.P
8.	Sandbed container (sand layer and underdrain pipe not shown)	Epoxy-based G.R.P
9.	Collection & oil removal tank c/w baffie and stainless steel strainner (not shown)	Epoxy-based G.R.P
10.	20 mm x 20 mm box section for support frame	Mild steel
11.	Centrifugal pump.	

Notes:

1. Wiring, piping and tubing details are not shown.
2. This figure is meant to give a conceptual perspective only

RESULTS AND DISCUSSION

WASTEWATER QUALITY

Table 2 shows the quality of wastewater generated at Malaya Electroplating Sdn. Bhd.

The Still Rinse Tank is the first rinsing tank after chromium plating. It is very acidic (average pH of 2.4) mainly due to dragout from the acidic chromium plating bath. Conductivity is high due to the large dragout containing Cr^{6+} and to a smaller extent other metals such as Zn, Fe and Ni. In certain samples, COD values were very high. Cyanide was also present at quite high concentrations on certain days.

The Flowing Rinse Tank is the last rinsing tank for Cr and Ni plated articles. Generally the pH of this wastewater is a round 7.0. The levels of COD, conductivity, Cl^-, SO_4^{2-}, Cr^{6+} and other metals, except Ni and Zn are generally quite low. On certain days CN was also detected.

Generally the wastes generated at the upstream discharge point (Figure 2 and Table 2) are moderate in COD, suspended solids, chloride, sulphate and Cr^{6+}. CN concentration was high due to dragout from Ni plating bath.

The Midline discharge point (Figure 2) had the highest concentration of Cr^{6+}, due to its location being nearest to the Cr plating operations and the lowest level discharge point. High concentrations of Ni and Cu are due to drip-washing of plated articles near this discharge point.

TABLE 2. Wastewater quality at Malaya Electroplating Sdn. Bhd. plant

	pH	Temp (°C)	Conductivity (mS/cm)	COD (mg/L	Suspended solid (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	CN^- (mg/L)	Cr^{6+} (mg/L)	Pb (mg/L)	Cu (mg/L)	Zn (mg/L)	Ni (mg/L)	Fe (mg/L)
(a) Still Rinse Tank	2.4 (2.2-2.7)	28.5	78.6 (36-171)	281.4 (27-950)	126.3 (78-164)	6.0 (0.8-21.8)	88.8 (5.0-225.0)	1.0 (0.08-4.25)	882.4 (721-1387)	0.3 (0.18-0.42)	5.0 (3.8-5.9)	18.7 (10.2-30.6)	10.4 (2.7-26.5)	8.8 (0.8-12.5)
(b) Flowing Rinse Tank	7.2 (7.1-7.3)	28.0	169.0 (162-178)	3.9 (1.1-10)	132 (117-142)	6.6 (4.9-7.2)	0.18 (5.1-35)	0.18 (0.02-0.46)	nd	0.11 (0.03-0.17)	0.52 (0.07-0.94)	22.1 (0.16-69.5)	5.6 (0.06-13.5)	0.09 (0.07-0.11)
(c) Upstream Discharge Point	4.6 (1.8-11.5)	27.6 (27-29)	873 (88-2460)	324 (150-530)	1100 (60-3220)	558 (40-2210)	4100 (500-9100)	42 (5-119)	0.76 (0.09-2.52)	0.94 (0.13-2.29)	5.3 (1.3-11.5)	107 (0.75-417.5)	954 (29.6-3375)	25.4 (6.6-60)
(d) Midline Discharge Point B	6.02 (3.1-7.4)	27.8	307.4 (45-848)	295 (155-380)	751.6 (500-1551)	162.4 (12.3-684)	610.0 (75-1000)	1.3 (0.6-3.2)	0.09 (0.08-0.10)	0.29 (0.07-0.59)	26.2 (0.7-96.8)	44.2 (40-49.5)	117.1 (18.5-286.0)	43.3 (4.0-114.5)
(e) Downstream Discharge Point	6.22 (4.8-7.5)	28	397.0 (0.22-578)	164.4 (30.1-222)	569.4 (54.1-950)	7.9 (3.1-14)	40.5 (0.4-60)	15.1 (0.3-50.1)	25.0 (0.3-76.8)	0.12 (0.06-0.18)	747.2 (0.14-2240)	24.3 (0.34-46.5)	728.8 (2.52-3500)	0.25 (0.05-0.64)

Removal of Hexavalent and Trivalent Chromium Preliminary experiments have shown that reduction of Cr^{6+} to Cr^{3+} is necessary to facilitate precipitation. The highest removal was obtained after coagulation with 40 mg/L polyaluminium chloride (PAC), at pH 9.0 and after 3 hours settling. Table 3 shows that under these conditions, there was complete precipitation of Cr^{3+} formed from Cr^{6+}.

TABLE 3. Removal of hexavalent chromium by precipitation after $FeSO_4$ addition, flocculation and settling

Sample Number	Influent [Cr^{6+}] (mg/L)	Effluent [Cr^{6+}] (mg/L)	Effluent [Cr^{3+}] (mg/L)	Percentage Removal
1.	4.84 ± 0.068	nd	nd	100%
2.	8.64 ± 0.050	nd	nd	100%
3.	13.76 ± 0.157	nd	nd	100%
4.	1.50 ± 0.009	nd	nd	100%
5.	61.85 ± 1.34	nd	nd	100%

nd: non-detectable

Removal of Cyanide Table 4 shows that complexation with $FeSO_4$ is crucial for removal of cyanide. In its presence, about 60% of cyanide was removed. Generally, the concentration of cyanide in the wastewater was rather low.

TABLE 4. Removal of Cyanide (CN)

Number	Method	Influent (CN) (mg/L)	Effluent (CN) (mg/L)	Percentage Removal
1.	Complexation of cyanide with $FeSO_4$, precipitation, flocculation and settling	(a) 0.03	0.03	0%
		(b) 0.06	0.02	67%
		(c) 0.03	0.01	60%
2.	Hydroxide precipitation, flocculation and settling only (no cyanide complexation)	(a) 0.01	0.01	0%
		(b) 0.01	0.01	0%
		(c) 0.01	0.01	0%

Removal of Metals other than Chromium A pH of 9.0 was selected to precipitate the metals as most metals including Ni, Zn, Cu, Cd and Cr would be precipitated down at pH between 8.5 - 11.0. Table 5 shows the removal of Cu, Ni, Zn, Fe and Pb at this pH either in the presence or absence of $FeSO_4$.

Generally, the addition of 40 mg/L PAC was as satisfactory as 50mg/L PAC. A period of three hours was necessary in most cases to settle all the

TABLE 5. Removal of metals other than Cr

Sample number	PAC added (ml)	Settling time (hr)	$FeSO_4$ addition (ml)		CU (mg/L)	Ni (mg/L)	Zn (mg/L)	Fe (mg/L)	Pb (mg/L)
				Std B EQ (SIE) R 1979	1.0	1.0	1.0	5.0	5.0
17c	40	3	No	Influent	0.02	2.24	0.17	nd	0.23
				Effluent	0.01	0.21	0.02	nd	0.20
				(% Removal)	(50%)	(91%)	(88.2%)	(-)	(13%)
18a	40	2	No	Influent	0.04	2.68	2.27	nd	0.22
				Effluent	0.01	0.13	0.02	nd	0.21
				(% Removal)	(75%)	(95%)	(93%)	(-)	(9%)
19a	40	15	No	Influent	0.02	1.54	0.25	nd	0.22
				Effluent	0.01	0.21	0.07	nd	0.20
				(% Removal)	(50%)	(86%)	(72%)	(-)	(9%)
20a	50	3	No	Influent	0.06	2.86	0.42	nd	0.22
				Effluent	0.01	0.23	0.04	nd	0.01
				(% Removal)	(83%)	(92%)	(90%)	(-)	(9%)
21b	50	2	No	Influent	0.02	5.91	0.22	nd	0.22
				Effluent	0.01	0.17	0.01	nd	0.01
				(% Removal)	(50%)	(97%)	(95%)	(-)	(95%)
22a	50	15	No	Influent	nd	2.53	nd	0.10	0.14
				Effluent	nd	0.29	nd	0.04	0.14
				(% Removal)	(-)	(89%)	(-)	(60%)	(-)
23a	40	3	Yes	Influent	0.14	2.36	0.37	0.09	0.28
				Effluent	0.01	0.16	0.01	0.41	0.32
				(% Removal)	(93%)	(93%)	(97%)	(-)	(-)
24a	40	3	Yes	Influent	0.05	2.10	0.26	0.11	0.38
				Effluent	0.02	0.10	nd	0.08	0.41
				(% Removal)	(60%)	(95%)	(100%)	(27%)	(-)
23c	40	3	Yes	Influent	0.42	3.33	0.50	0.77	0.43
				Effluent	0.02	0.08	0.07	0.20	0.37
				(% Removal)	(95%)	(98%)	(86%)	(74%)	(13%)

nd: non-detectable

flocs formed. There is generally good removal of Cu, Ni and Zn. The presence of $FeSO_4$, added as a reducing agent to convert Cr^{6+} to Cr^{3+}, does not contribute significantly towards precipitation of other heavy metals.

CONCLUSION

A sequencing batch process utilising a Two-tank System and using lime and ferrous sulphate was found to be effective in removing hexavalent and trivalent chromium, cyanide and other metals from metal finishing wastewater. The highest removal of Cr^{6+} was obtained after reduction to Cr^{3+}, coagulation with 40 mg/L PAC at pH 9.0 and left to settle for three hours. Complexation with $FeSO_4$ was crucial for cyanide removal. At pH 9.0, most metals were also generally well removed to meet the Standard B limits of the Environmental Quality (Sewage and Industrial Effluent) Regulation 1979.

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REFERENCES

1. DOETH. 1985. *Report on Toxic and Hazardous Waste Survey in Malaysia.* Kuala Lumpur: Jabatan Alam Sekitar, Malaysia.

2. Teh L. H. 1980. *Wastewater Survey Report.* Kuala Lumpur: Department of Environment, Malaysia.

3. American Public Health Association (APHA). 1976. *Standard Methods for the Examination of Water and Wastewater,* 14th ed., Washington, APHA.

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