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Development of a Precipitation Based Separation Scheme for Selective Removal and Recovery of Heavy Metals from Cadmium Rich Electroplating Industry Effluents

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Abstract: The treatment of electroplating wastes is a serious worldwide problem, because of their high content of many different heavy metals. Chemical precipitation based treatment methods could be an important alternative for fractional selective separation of heavy metals if they are systematically developed by sequencing of pH, adjusting the added portions of precipitating agents, and selecting the optimum time period before removing the precipitate from the solution. In this study, for selective removal and recovery of Cd from real electroplating bath wastewater (containing high amounts of Cd, medium amounts of Zn, Cu, Fe and small amounts of Ni, Co, Mn), a precipitation based separation scheme was developed. The scheme comprised of three consecutive steps: 1) Acid treatment with nitric acid (HNO_3). Cyano-metal complexes were decomposed in acidification step and complete removal of iron was achieved. 2) Alkali precipitation by sodium hydroxide (NaOH). Large portion of Cd was recovered as pure $Cd(OH)_2$. 3) As a polishing step sulfide precipitation by sodium sulfide (Na_2S) was applied. pH was the critical parameter in sulfide precipitation. Addition of sodium sulfide in alkali pH range led to cadmium precipitation whereas copper was totally precipitated in acidic pH range. The sulfide precipitation step may be replaced by more environmentally friendly steps

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(e.g. polymer enhanced ultrafiltration) until the heavy metal concentrations were reduced down to suitable discharge limits.

Keywords: Hydroxide precipitation, sulfide precipitation, heavy metal removal, cadmium, iron, copper, electroplating waste

INTRODUCTION

According to 1986 estimates of the Environmental Protection Agency, cadmium is used primarily for metal plating and coating operations (35%), including transportation equipment, machinery and baking enamels, photography, and television phosphors. It is also used in nickel-cadmium and solar batteries (25%), in pigments (20%), as a stabilizer in plastics and synthetic products (15%), alloys and other uses (5%).

In spite of its toxic nature and high cost, cadmium plating is preferred because of its ability to provide a corrosion protective coating with an attractive appearance on various basis metals, especially on iron and steel. Due to the relatively high price of cadmium, it is largely applied in the form of thin coatings. Aircraft, marine, and military outdoor uses are common. The electrical industry makes use of Cd-plate on steel and other metals because it is easily soldered and has low contact resistance. Cadmium plating is often used on parts of assemblies consisting of dissimilar metals, such as steel and brass to minimize the galvanic corrosion (1).

The most important complexing ions in cadmium electroplating are the cyanides. Cadmium-cyanide bath has the ability to give a dense, fine-grained deposit, which may be made highly lustrous and reflective. Therefore the cyanide bath is used almost exclusively for commercial cadmium-plating (1).

Wastewater produced during electroplating is one of the main causes of contamination of the natural environment with metal ions. Their composition and quantity depends on the type of chemical operations carried out, size and shape of the surfaces, and on the washing system applied (2). The negative impact of waste streams containing heavy metals upon the environment, gives rise to increasingly strict regulations. Especially the toxicity of cadmium is recognized by the U.S. Environmental Protection Agency, which has limited this metal in drinking water to a maximum of 10 $\mu g/L$ (3). According to recent regulations of EPA, for common metals facilities discharging 38000 liters or more process wastewater (resulting from the process in which a ferrous or nonferrous basis material is electroplated with copper, nickel, chromium, zinc, tin, lead, cadmium, iron, aluminum, or any combination thereof) per day should obey the limitations listed in Table 1 (4).

Amoung the industrial waste effluents containing heavy metals, treatment of electroplating wastes is a serious worldwide problem, because of their high content of economically valuable heavy metals. In addition to metal ions and counter anions that are present in synthetic wastewaters, surfactants, brighteners, organic and sometimes inorganic addition agents are also present in

Table 1. Common metals facilities discharging 38000 liters or more per day pretreatment standards for existing sources limitations (mg/l) (4)

Pollutant	Maximum for any 1 day	Average of daily values for 4 consecutive monitoring days shall not exceed
Cu	4.5	2.7
Ni	4.1	2.6
Cr	7.0	4.0
Zn	4.2	2.6
Pb	0.6	0.4
Cd	1.2	0.7
Total metals	10.5	6.8

industrial waste effluents. Because of the complex nature of commercially discharged waste effluents, none of the widely used methods is sufficient for complete fractional separation of metals. Various alternative processes have been developed for the removal and recovery of heavy metals such as adsorption, precipitation, liquid–liquid extraction and ion-exchange (5). The main disadvantages of the ion-exchange method are high resin cost, solvent wash-out for impregnated resins, and slow operation rate. High amount of solvent losses, requirement of high capital costs, phase disengagement difficulties, and large inventory of the solvent are the main drawbacks of solvent extraction (6). Requirement of large number of stages for effective removal of heavy metals makes the adsorption process uneconomical and presence of other metals may reduce the efficiency of adsorption process (7). Also most of these methods are only suitable for low metal concentrations (8–11), which means that they may only be applied as a polishing step.

Precipitation of heavy metals with lime, sulfide, and caustic soda are the most commonly used simple methods for metal removal. However, heavy metals can not be removed completely by hydroxide precipitation. Higher degrees of removal can be achieved by sulfide precipitation, but in this case high volumes of toxic sludges which are difficult to dispose are produced (12). It was reported that values of pH 9.5 or greater are necessary for effective precipitation of Zn, Mn and Mg as hydroxide with lime treatment. But the same procedure may be unsatisfactory for Cd and the use of sulfide for Cd precipitation appears to be necessary (13). By controlling the sulfide level metals can be precipitated selectively by taking into account the fact that every precipitating metal has a unique pS level for sulfide precipitation which is directly related to its solubility product (14). Many of the precipitation studies in literature are carried out by using single or binary metal containing solutions (15, 16), or simulated (only metal content wise) synthetic wastewaters was employed (17), overlooking some complexities of real wastewaters.

A more sustainable and effective method could be rectified for heavy metal removal and recovery if a process scheme which can achieve selective separation of metals and produce reusable pure metal sludges could be developed. This process scheme may be developed by pH sequencing with the optimization of parameters like added doses and kind of precipitating agents, and the waiting period before removing the precipitate from solution.

Although it is generally used as a stand alone method (15, 18) chemical precipitation, when it is systematized properly, can be very appropriate as a first step of a hybrid separation process. Precipitation of sparingly soluble metal compounds followed by micro- or ultrafiltration (19), bioaccumulation and microfiltration (20), and precipitation followed by polymer enhanced ultrafiltration (21) are amoung the possibilities as the second step of the hybrid processes.

In this study, wastewater samples were taken from industrial electroplating bath of a local company which operates batch wise and have a pH value of approximately 13. Different pieces such as steel, iron, bronze are coated by Cd in the same bath, therefore the content of pollutants (dissolved, colloidal, or in suspension), and the concentration of heavy metals in wastewater may vary with time. Because of the complex nature of the selected solution, fractional separation of heavy metals by simple and economic water treatment methods is difficult. The objective of this study is to develop a precipitation based scheme to investigate its potential for selective removal, recovery, and reuse of heavy metals from cadmium dominated industrial electroplating baths and also to asses its potential as a first step of a hybrid process scheme. By developing a suitable algorithm, it is aimed to recover heavy metals to be used commercially.

EXPERIMENTAL SECTION

Characterization of Wastewater Sample

In order to get rid of suspended particles in the waste stream, dead-end prefiltration was performed with Nucleopore Vacuum Filter and after each precipitation step, the precipitated part is removed from the solution by Schleicher&Schuell/GF 52 Glasfaser Rundfilter, having a pore size of 1 μm.

For the determination of the metal content of the solution, samples were first analyzed by Direct Reading Echelle Inductively Coupled Plasma (DRE ICP) (Leeman Labs Inc.). Routine analyses were made by Flame Atomic Absorption Spectrophotometer (FAAS) (Philips, PU9200X).

Experimental Schemes

Step 1: Acidification Experiments

After prefiltration, pH of the sample was reduced by adding nitric acid (HNO_3 Merck (Etwa 60%, extra pure)). Acid was added either in 5 ml (small doses) or in 25 ml (large doses). While adding acid to the solution, the pH was controlled continuously by a pH meter (WTW pH330) and the solution was stirred at a rate of 250–300 rpm. After acidification, the solution was filtered to remove precipitate from solution.

Step 2: Alkalination Experiments

After acidification, the pH of the solution was increased by adding 1 M sodiumhydroxide solution (NaOH). Sodiumhydroxide solution was prepared by dissolving sodium hydroxide pellets (Merck) in ultra-pure water produced by the Millipore 'Milli-Q Plus' system (resistance of 18.2 $M\Omega cm^{-1}$). Sodiumhydroxide was added either in 10 ml (small doses) or by 100 ml (large doses).

While adding NaOH to the solution, the pH was controlled continuously and the mixture was stirred at a rate of 250–300 rpm. After alkalination, the solution was filtered to remove the precipitate from the solution.

Step 3: Sodium Sulfide (Na_2S) Addition

After the alkalination step, Na_2S was added as ground solid particles to the solution. The reason for ground solid addition is to keep the treated volume at minimum level. While adding Na_2S to the solution, the pH was controlled continuously by the pH meter and the mixture was stirred at a rate of 250–300 rpm.

After the addition of sodiumsulfide the solution was filtered to remove the precipitate from the solution.

RESULTS AND DISCUSSION

As expected, Cd concentration of the electroplating waste effluent selected for this study is very high as compared to other metals. Iron (Fe), zinc (Zn), and copper (Cu) are found in lower concentrations, and also trace amounts of nickel (Ni), cobalt (Co), and manganese (Mn) exist. Average compositions of wastewater samples were determined and tabulated in Table 2. Representative samples were taken from the bath at different months of the year. Depending on the type of chemical reactions carried out, the basic material of the coated surfaces and on the washing system applied, the quantity and composition of the samples were found to change.

Typical cadmium electroplating baths were prepared by sodium cyanide (NaCN), cadmium oxide (CdO). 1.5–2.0 pounds of zinc dust is added per 100 gallons of solution and sodium hydroxide (NaOH) is added to improve solution conductivity (1). Cd content of commercially used electroplating bath is in the range between 1000–3000 mg/l (22), and concentrations found in this study are in this range. The Cd content of the initial wastewater

Table 2. Composition of the wastewater sample

	Concentration (mg/l)	Weight % (dry basis)
Cd	28656 ± 2818	97.3
Cu	177 ± 14.7	0.6
Fe	233 ± 11.9	0.79
Zn	280 ±33	0.95
Ni	61 ±16.8	0.2
Co	0.59 ± 0.49	0.001
Mn	1.13 ± 0.76	0.001

used in this study was much larger than those considered in previous studies (23–25), but the content of other metals were similar.

Eleven different methodologies (details are given in Fig. 1), with different parameters and paths were developed in three consecutive precipitation stages. In order to see the effect of the rate of acidification and alkalination on the precipitation, different dosages of HNO_3 and NaOH were added. The aging of the precipitate may be disadvantageous because it may reduce the efficiency of the precipitation by resolvation. To investigate this possibility, the effect of the time interval before the filtration of the solution is varied by considering two alternatives:

1) Removal of the precipitate immediately
2) Removal of the precipitate after waiting for 12 hours.

Results of Acidification Experiments

Metal complexes in the wastewater sample were decomposed and precipitated in the acidification step. The rate of decomposition of metal complexes in solution and precipitation can be controlled by pH sequencing and by controlling the HNO_3 addition rate.

As indicated in Fig. 1, acidification starts at pH 13 and HNO_3 was added either in small or large doses. As a first alternative for pH sequencing, pH is reduced from 13 to 6, where cloudy sediments start to form, then at pH 6 the precipitated part was removed by filtration, a sample was taken from the solution for metal analysis, and the rest of the solution is acidified down to pH 1. As a second alternative for pH sequencing, the pH of the solution is directly reduced from pH 13 to pH 1 by either small or large dose acidification.

At the end of the acidification, an insoluble precipitate in a dark purple color was obtained. Bearing in mind the colors of the metallic compounds, it may be said that the main constituents of this precipitate were iron nitrate (violet), manganese nitrate (purple), and cobalt nitrate (red) (26), which was

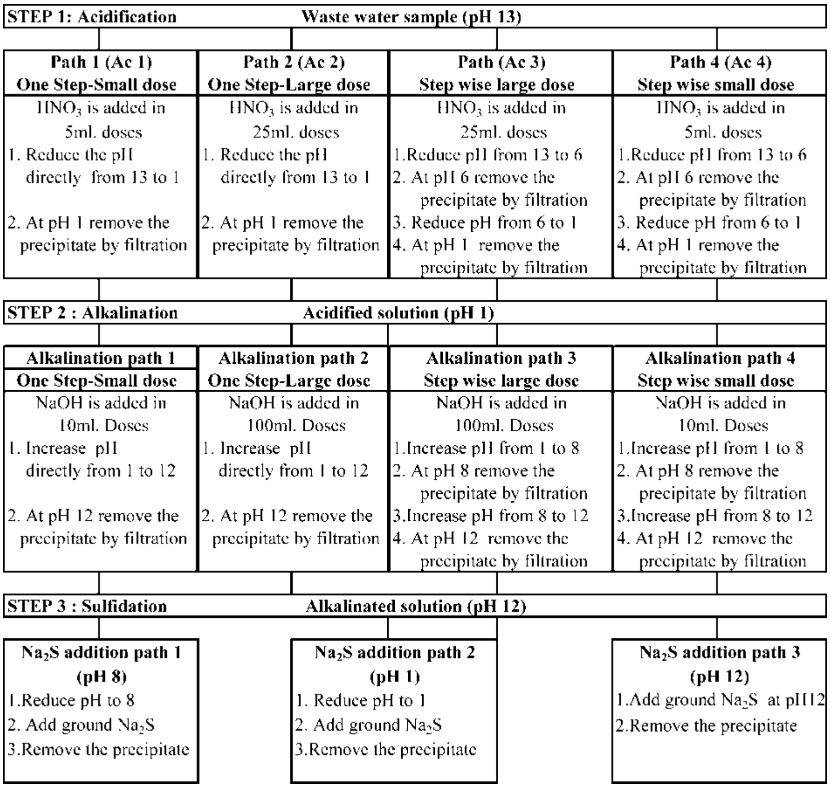

Figure 1. Schematics of acidification and alkalination experiments.

consistent with the results obtained by making the elemental analysis of the solution by AAS after acidification step.

Consequences of the pH sequencing and HNO_3 addition rate can be explained as follows: Co and Mn impurities and Fe was completely removed at the early stages of the acidification step (Table 3). Since these metals were completely removed along all paths, the effect of acidification parameters were not important for these metals.

The solubility of iron nitrate (87 g/100 g water) is low as compared to the solubility of cadmium nitrate (159 g/100 g water) (26), Fe was precipitated rapidly at the beginning of the acidification. For Cd, Zn, Cu, and Ni, the acidity level at pH 6 may not be sufficient for the decomposition of the metal complexes, therefore the reduction of pH was found necessary for effective precipitation of these metals (Fig. 2).

The dosage of HNO_3 effects the recovery of Cd, Zn, Cu, and Ni. As shown in Fig. 3, by adding HNO_3 in small dosages higher recoveries were obtained for these metals. The dosage of HNO_3 mostly effects the recovery of Cd as compared to Zn, Cu, and Ni. For instance, in case of one-step acidification,

Table 3. Concentrations and percent recoveries of Fe, Co, and Mn after acid treatment

Metal	Initial concentration (mg/l)	After acidification path 1 Concentration (mg/l)	Recovery (%)	After acidification path 4 Concentration (mg/l)	Recovery (%)
Fe	94	0.06	100	0.05	100
Co	0.6	0	100	0	100
Mn	1.12	0	100	0	100

approximately 39% of Cd was recovered whereas this value drops to 4% when large dose acidification was applied (Fig. 3). This difference may be due to the mechanism of the decomposition of Cd complexes. It is known that, with a very concentrated solution and a compound of very low solubility, a large number of crystals with small dimensions are formed, and precipitation is rapid. On the other hand, if the solution is dilute and if the compounds are more soluble, crystals of relatively large dimensions are obtained, and precipitation is slow (27).

By comparing the recoveries obtained in a single step and step-wise acidification, it can be seen that, by applying step-wise acidification higher recoveries can be obtained (Fig. 4). This means that the removal of the precipitate formed at the intermediate step (pH 6) and further reduction of pH to 1 enhances the precipitation.

As a result of acidification, independent of rate of acidification, the third main constitute of the electroplating bath (Fe) was completely removed (Table 3). Approximately half of the other contaminants (Zn, Cu, Ni) were also removed at that stage and Cd remains mostly in the effluent.

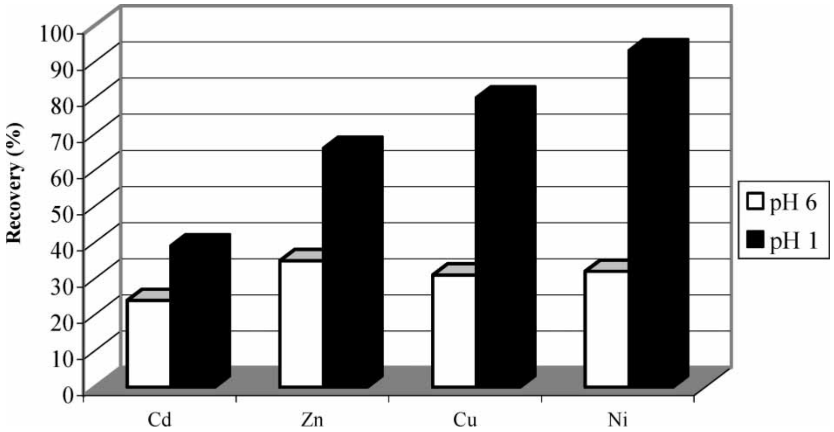

Figure 2. Effect of acidification pH on recoveries.

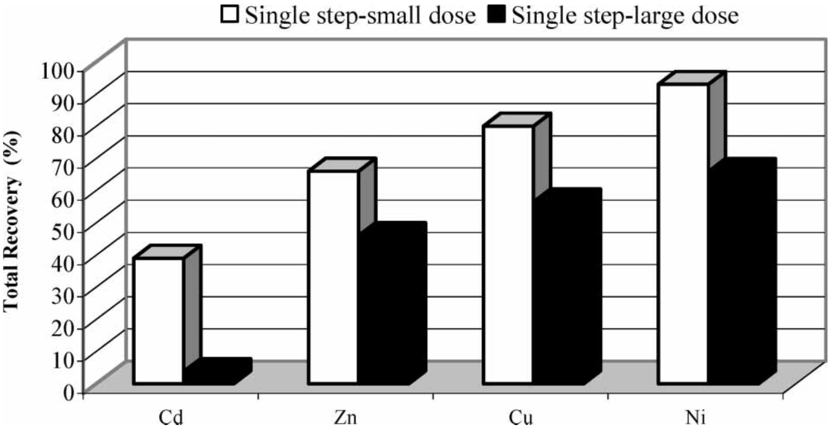

Figure 3. Effect of dosage of HNO_3 in single-step acidification.

Low recovery of Cd and total removal of Fe in the acidification step may lead to the selective fractional precipitative recovery of metals. By choosing the acidification path (i.e, rapid reduction of pH from pH 12 to pH 1 in large doses), Fe and approximately half of the other contaminants (Zn, Cu, Ni) can be removed from the solution at the early stages of acidification and Cd can be recovered in the later steps following acidification.

Results of Alkalination Experiments

By reducing the pH down to 1, cyano-metal complexes were decomposed, and metal concentration of the wastewater was decreased. For further reduction in

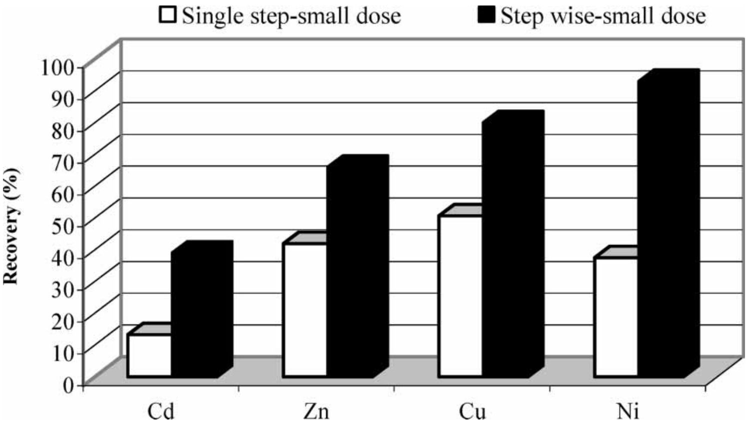

Figure 4. Comparison of single step and step-wise small dose acidification.

metal concentrations, alkali-precipitation was carried out by following four different paths (Fig. 1). NaOH was added as 0.25 M or as 1 M solutions, the addition of dilute NaOH (0.25 M) did not affect the results but it ends up with an undesirable increase in the volume of the treated solution, therefore using the 1 M NaOH solution was preferred.

As in the case of acidification, pH sequencing and addition rate of NaOH are important parameters. In Fig. 5, stage recoveries of metals at pH 8 and at pH 12 during alkalination are shown. There are considerable differences in the stage recoveries of all metals depending on the alkalination path followed. When alkalination pH was 8, use of large doses increased the recoveries whereas when precipitation pH increased to 12, the effect of the dosage is completely reversed. When small doses were used higher pH values were better for precipitation. However when large doses were used in the lower pH region, better precipitative recoveries were obtained.

Theoretical solubility data usually can not be used in practice due to the presence of other ions, and in literature there are experimental studies related to the single metal precipitation behaviors (12). The idea behind the hydroxide precipitation is the addition of the precipitation agent, usually to the pH of minimum solubility, but this approach has limitations in cases where more than one metal is present. The pH of minimum solubility for Cu and Zn is reported to be around 8.5, for Ni around 10, and for Cd the minimum solubility is achieved approximately at pH 12. It was also reported that the solubility of CuS in alkali range is low as compared to other metals (12, 26). Keeping in mind this precipitation behavior of Cu, Zn, Cd, and Ni, the results of the alkalination experiments may be explained as follows:

In case of large dose alkalination, stage recoveries of all metals at pH 8 were higher than the recoveries obtained at pH 12, which is consistent with the fact that minimum solubility occurs at the pH range around 8–9 for metals other than Cd. For efficient precipitation of Cd, the pH should be

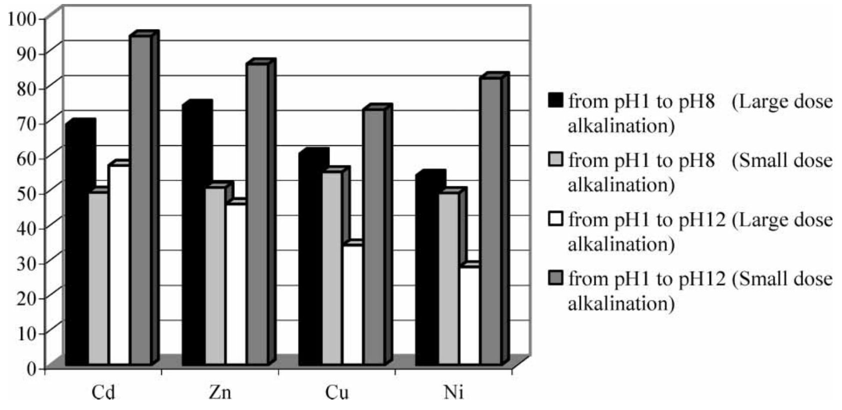

Figure 5. Stage percent recoveries in different alkalination steps.

increased further. When this increase occurs rapidly due to a large dose addition of NaOH, Cd precipitation was not efficient as expected. In small dose alkalination, the best percent recoveries were obtained while increasing the pH directly from pH 1 to 12. In that case, a considerable amount of Zn, Cu, and Ni precipitated at pH around 9, and a gradual increase of pH to 12 gives rise to the efficient precipitation of Cd (Fig. 5).

During alkalination a stable white precipitate formed at the pH level of approximately 12. The precipitate was removed from the solution by vacum-filtering. The cake obtained after the filtration was dried in the oven at 100°C for 18 hours. A representative sample of the dried material was characterised by X-ray diffractometer (Philips PW 1729). As demonstrated in Fig. 6, the precipitate was identified as cadmiumhydroxide $Cd(OH)_2$.

Production of $Cd(OH)_2$ is important because, by heating $Cd(OH)_2$ at 350°C cadmiumoxide (CdO) can be obtained. CdO is widely used in the electroplating industry for the preparation of the cadmium-cyanide electroplating bath (28).

In order to examine the purity of $Cd(OH)_2$ samples, metal analyses were made by FAAS. As can be seen in Table 4, irrespective of the alkalination path followed, almost pure $Cd(OH)_2$ was obtained. Due to the relatively high price of Cd, the recovery of this metal as $Cd(OH)_2$ may be considered as a success of the developed separation scheme.

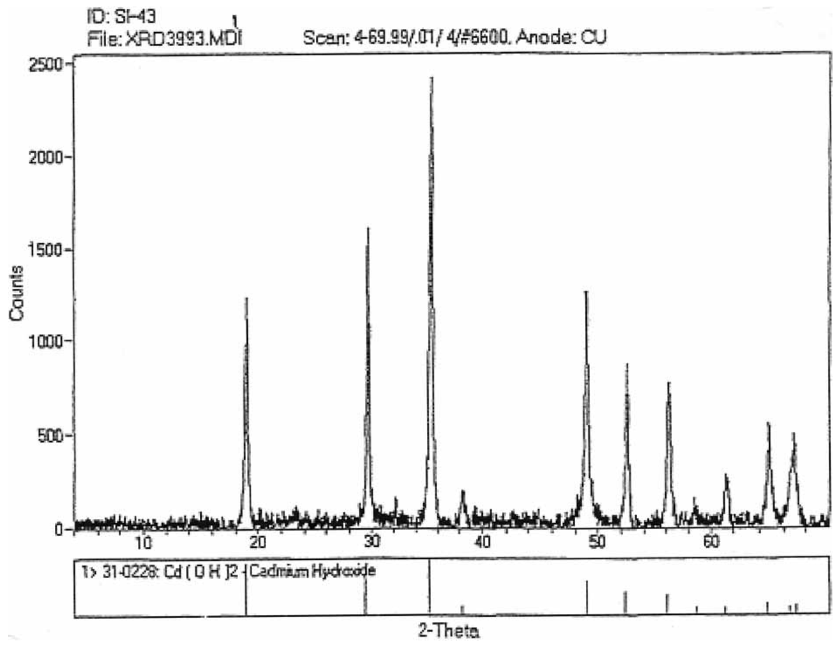

Figure 6. Result of X-ray analysis.

Table 4. Compositions of recovered solids at the end of four different alkalination paths

	Weight percent (%)			
	Small dose	Small dose (step wise)	Large dose	Large dose (step wise)
Cd	99.54	99.30	99.40	98.90
Zn	0.14	0.36	0.20	0.50
Cu	0.08	0.03	0.10	0.20
Ni	0.12	0.13	0.10	0.20

Effect of Time on the Recovery of Metals

After each acidification and alkalination step, treated solution was filtered in order to separate the precipitate formed from the solution. Filtration was made either after a waiting period of 12 hours or after waiting only one hour.

According to the experimental results it is apparent that the filtration of the solutions immediately after acidification and alkalination gives higher recoveries than those samples kept for one night after precipitation especially for Cd which is the main constituent of the waste sample (Figs. 7, 8). For Fe, irrespective of the time before filtration, complete removal was achieved. As seen in Figs. 7 and 8, the same trend was observed in both acidification and alkalination steps. The reason may be explained as follows: as time passes, solid precipitates may dissolve back into the solution thereby reducing the

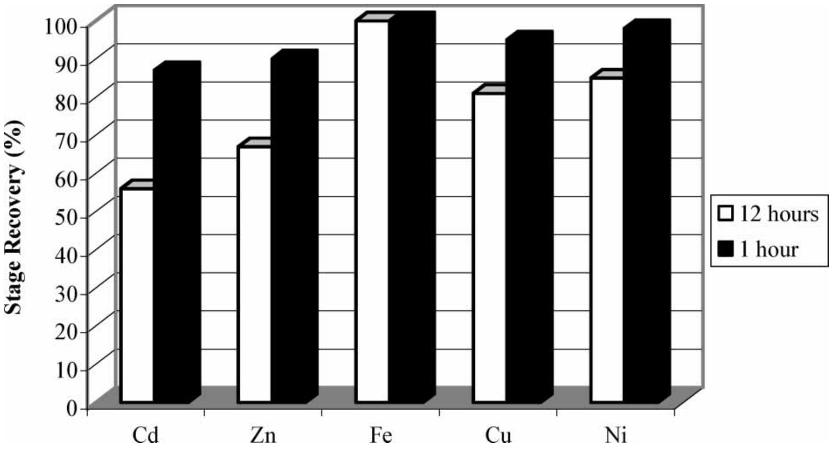

Figure 7. Effect of time duration on the recovery of heavy metals in acidification steps.

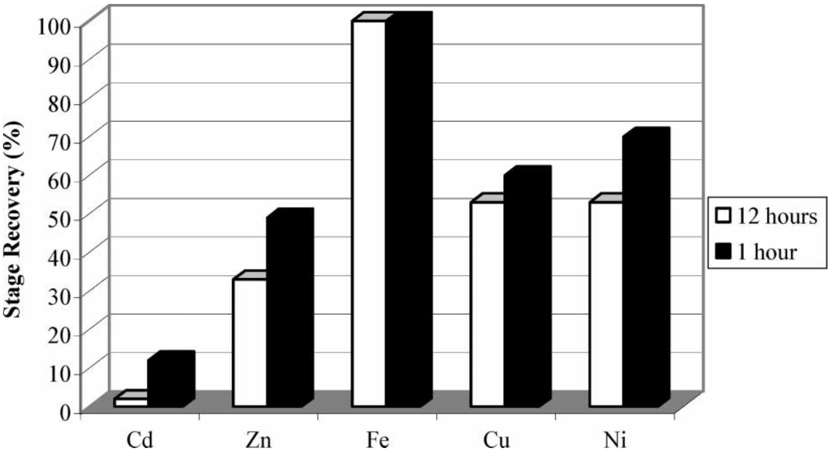

Figure 8. Effect of time duration on the recovery of heavy metals in alkalination steps.

percent recovery of the metals or poor and indiscriminant metal binding may often result in unstable metal–ligand precipitates which can decompose and release the metals back into the environment over varying, but usually short, periods of time (29).

Strategy for Maximum Recovery of Cadmium in Acidification and Alkalination Steps

A suitable strategy that gave the maximum recovery was large dose step-wise acidification from pH 12 to pH 1 and after that, small dose single step alkalination from pH 1 to pH 12. In both steps, immediate filtration after precipitation was carried out. By choosing this strategy in the acidification step the third main constituent (Fe) of the solution and Co, Mn impurities were removed at the early stages of acidification, Ni, Zn, and Cu complexes were decomposed and precipitated to some extent, whereas most of the Cd remains in the solution and Cd can be recovered as pure $Cd(OH)_2$ in alkalination steps.

Concentrations of metals at different stages of precipitation experiments are given in Table 5. As is seen at the end of alkalination, considerable amounts of Cd, Zn, Ni, and Cu still remained in the solution, in order to reduce the concentrations of these metals further down, sulfide precipitation was applied.

Results of Sulfide Precipitation Experiments

Typical analyses results of some selected samples after sulfide precipitation are given in Table 6. Na_2S addition was applied at neutral, acidic, and basic medium

Table 5. Typical concentrations of metals in the selected sample at different stages of the experiments

	Concentration (mg/l)		
Sample 1	Original sample (pH ~ 13)	After acidification (pH 1)	After alkalination (pH 12)
Cd	24800	24200	6700
Cu	288	81	30
Fe	248	0	0
Zn	130	72	29
Ni	53	40	15
Co	1.75	0	0
Mn	2.25	0.5	0

in order to see the effects of pH. Ground Na_2S was preferred to keep the treated volume and hence the waste sludge production at a minimum.

It was reported that the CuS solubility in alkali condition is very low (12), but by looking at the concentration values of Cu in treated-water (Table 6), it can be concluded that the solubility of CuS in alkali condition is higher than the acidic condition. This may be explained as follows: separation of CdS from sulfide precipitates of other elements is based upon its solubility in dilute acid. It is also known that copper sulfide is a very insoluble compound and the presence of soluble sulfide ion causes the precipitation CuS. Considering this fact, the behavior of Cu at low pH values can be explained as follows: CdS becomes soluble in acidic range that increases the concentration of S^{2-} ion in the solution. Consequently the presence of S^{2-} ion enhances the formation of CuS which precipitates due to its low solubility (28).

As in the case of acidification and alkalination steps, pH is an important factor in sulfide precipitation. The addition of sodium sulfide (Na_2S) in alkali pH range leads to Cd precipitation while most of the Cu remains in the solution. On the other hand, when Na_2S is added in acidic pH range, considerable amounts of Cd remains in the solution while Cu is totally precipitated and eliminated. This result is consistent with the literature: For CuS the pH point for minimum solubility is in the acidic pH range, but that of CdS in the alkali pH range. By adjusting the initial value of the pH, fractional precipitation can be made according to the desired product. In order to obtain Cd-rich solutions, Na_2S should be added in acidic pH range. If the Cu-rich solution is the desired product, sulfide precipitation should be performed in an alkali pH range.

In sulfide precipitation, two different paths may be followed:

1) Limited amount of sulfide can be added until metal concentrations suitable for consecutive polishing steps was reached.

Table 6. Reduction of metal concentrations by sulfide precipitation

Before Na_2S precipitation conc. (mg/l)				Added Na_2S (g)/ 10 ml sample	After Na_2S precipitation							
					Conc. (mg/l)				Recovery (%)			
Cd	Zn	Cu	Ni		Cd	Zn	Cu	Ni	Cd	Zn	Cu	Ni
At pH 12												
7500	18	86	6	0.25	10	5.5	60	5	99.9	67	30	17
9500	27	126	15	0.45	12	28	80	8	99.9	70	37	47
1025	15	103	4	0.15	0.5	6.6	77	2	99.9	53	25	50
6500	9	35	4	0.25	0.5	1.2	29	3	99.9	88	17	25
2000	11	27	6	0.35	0.3	0.5	25	4	99.9	90	7	33
At pH 1												
6700	29	30	15	0.20	70	25	0	9	98.9	14	100	40
7500	26	72	6	0.30	205	14	0	6	97.3	46	100	0
9500	27	126	15	0.40	1850	15	2	6.5	80.5	44	98.5	47
At pH 8												
8500	20	119	8	0.30	8	13	7	8	99.9	35	94	0
9500	27	126	15	0.40	10	16	5	0	99.9	41	96	100

2) Sulfide precipitation can be repeated until the metal concentrations in the solution approach to acceptable discharge limits.

If the aim is to remove the heavy metals from solution, precipitation steps can be repeated. In that case metals are removed as a mixture of metal salts. In this study, it was preferred to continue with the chemical precipitation treatment in order to reduce the metal concentration down to suitable discharge limits. At the end of sulfide precipitation, a yellow colored precipitate was obtained and characterized by X-ray diffractometer (Philips PW 1729). It is known that, cadmium sulphide can have colors varying from lemon yellow to orange and red (28). By looking at the physical properties and the X-ray analyses results the precipitate obtained can be easily identified as CdS.

As a second alternative: consecutive polishing steps may be used after sulfide precipitation. Although it is generally used as a stand alone method, chemical precipitation, when it is systematized properly, can be very appropriate as a first step of a hybrid separation process. Biosorption, electrodialysis (30), polymer enhanced ultrafiltration (31) may be suitable alternatives for polishing steps. For instance, Cd and Cu can be further recovered separately by applying polymer enhanced ultrafiltration after precipitation steps.

Summary of the Results of the Precipitation Scheme

A brief summary of the results obtained in this study is as follows: At the end of acidification, a complete separation of Fe was achieved whereas the Cd precipitation was not very significant. Approximately 50% of Zn and between 66–97% of Ni and Cu were removed in the acidification step. At the end of the alkali-precipitation, almost pure $Cd(OH)_2$, which can be recycled for the preparation of Cd-cyanide electroplating bath, was obtained. Depending on the acidification and alkalination paths followed, between 49–70% of the Cd is recovered as cadmiumhydroxide $Cd(OH)_2$. As far as the compound CdS obtained at the end of the sulfide precipitation is concerned, total recovery yields of the usable compounds ($Cd(OH)_2 + CdS$) are found to be approximately 100%. It was observed that considerable amounts of Cd, Zn, Ni, and Cu still remained in the solution at the end of the alkalination step.

In acidification and alkalination steps, higher metal recoveries could be reached by immediate removal of the precipitate from the solution.

The pH was the critical parameter in sulfide precipitation and by adjusting the pH, solutions with high Cu or Cd content can be obtained.

CONCLUSION

It can be concluded that by adjusting the precipitation parameters (pH sequencing, time, and dosage of precipitation agents) a selective separation and recovery of heavy metals from industrial wastes can be achieved.

Depending on the composition of the wastewater and the desired end product, precipitation schemes may be developed. In this study, Cd dominated wastewater was used. Contaminants of the wastewater (Fe, Cu, Ni, Zn) and impurities (Co, Mn) were removed by selecting the pH for minimum solubility for these metals. Cd was recovered as pure $Cd(OH)_2$, which is a valuable compound.

Process sequencing can be suggested for the removal and recovery of heavy metals, especially for Cd, from electroplating waste effluents. By keeping sulfide addition to a minimum developed scheme can be used as a first stage of a hybrid process to eliminate heavy metals completely.

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