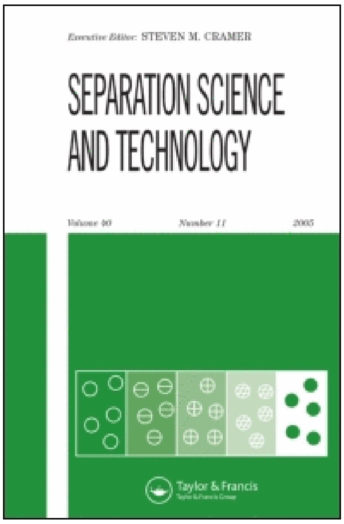

Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Removal of Toxic Metal Ions from Metal-Finishing Wastewater by Solvent Extraction

Curtis W. Mcdonald[a]; Raghbir S. Bajwa[a]
[a] DEPARTMENT OF CHEMISTRY, TEXAS SOUTHERN UNIVERSITY, HOUSTON, TEXAS

To cite this Article Mcdonald, Curtis W. and Bajwa, Raghbir S.(1977) 'Removal of Toxic Metal Ions from Metal-Finishing Wastewater by Solvent Extraction', Separation Science and Technology, 12: 4, 435 — 445

To link to this Article: DOI: 10.1080/00372367708058088

URL: http://dx.doi.org/10.1080/00372367708058088

SEPARATION SCIENCE, 12(4), pp. 435–445, 1977

Removal of Toxic Metal Ions from Metal-Finishing Wastewater by Solvent Extraction

CURTIS W. McDONALD and RAGHBIR S. BAJWA

DEPARTMENT OF CHEMISTRY
TEXAS SOUTHERN UNIVERSITY
HOUSTON, TEXAS 77004

Abstract

Solvent extraction procedures are presented for the removal of chromium, cadmium, and zinc from metal-finishing wastewater. The procedures utilize a 25% Alamine 336–xylene solution as the extractant. The three metals can be extracted selectively or simultaneously using a 100 to 1 aqueous phase to organic phase ratio. All three metals can be stripped from the organic phase with better than 99.5% efficiency with 4 *M* NaOH. The regenerated reagent can be recycled and reused without any loss of extraction efficiency. The procedures are reproducible, rapid, and simple.

INTRODUCTION

As a result of our increased awareness in recent years of the importance of protecting and improving the quality of our water, there has been considerable interest in treating polluted waters generated by various industrial processes. Due to this concern, new technology has been developed and is currently available to remove toxic materials from polluted water at reasonable cost for many industrial processes; thereby preventing the pollution of our rivers, streams, and municipal sewer systems.

The metal-finishing industry is one in which sufficient technology is not generally available for the economic removal of toxic materials from the wastewater it generates.

There are more than 15,000 metal-finishing facilities in the United States. Of these, more than 10,000 can be classified as small shops. Ample technology is available at reasonable costs for huge operations such as large independent plants and captive facilities. The captive facilities are generally subsidiaries of automobile, home appliance, or plumbing manufacturing companies. The technology currently available to remove toxic metals from metal-finishing wastewater requires an extensive capital outlay for equipment. This eliminates the utilization of the available technology by the small shops for economic reasons. Since the vast majority of the metal-finishing facilities are in the small shop category and are generally concentrated in industrial areas within cities, they pose a serious pollution problem for municipal sewer systems.

This paper describes the use of solvent extraction procedures using high-molecular-weight amines to detoxify metal-finishing wastewater. Solvent extraction methods using high-molecular-weight amines for the removal from aqueous solutions of the toxic metal ions generally found in metal-finishing wastewater, such as cadmium, chromium, copper, nickel, and zinc, have been extensively investigated (*1–10*). Some extraction processes have been recommended for utilization by various industries for water detoxification (*11, 12*). Several industrial processes utilizing solvent extraction procedures have recently been employed in Europe (*13*). The Gullspang process utilizes the high-molecular-weight amine Alamine 336 to remove molybdenum, tungsten, chromium, iron, cobalt, and nickel from solid waste such as scrape, lathe turnings, and mill shavings. The Soderfors process is used to recover metals and acids from a stainless steel pickling bath. The Valberg process is currently being used to recover zinc from effluent water generated by the manufacture of rayon. All of these processes utilize solvent extraction procedures on an industrial scale.

EXPERIMENTAL

Apparatus

A NaI(Tl) well-type scintillation counter, 1.75 × 2.0 in., consisting of a high voltage power supply, a discriminator, and a timer scaler was used for gamma counting.

A Perkin-Elmer Model 360 atomic absorption spectrophotometer equipped with digital display and a Houston Instruments OmniScribe recorder was used to analyze both phases for the metals. Oxygen and acetylene gases were used for the flame.

A Dorhmann Model DC-50 Total Organic Carbon Analyzer was used to analyze the aqueous phases for loss of reagent from the organic phases during the extraction processes.

A Sargent Welch Model 119NX digital pH meter was used to make the pH measurements.

High-speed motors equipped with glass paddle stirrers were used to mix the phases.

A clinical centrifuge with 50 ml heavy walled glass centrifuge tubes was used for phase separation.

Reagents

Primene JM-T is a mixture of amines principally in the C_{18-22} range.

Primene 81-R is a mixture of amines principally in the C_{12-14} range.

Amberlite LA-1 (impure *n*-dodecenyltrialkylmethyl amine) is a secondary amine. Amberlite LA-1 and the primary amines listed above are available from Rohm and Hass Chemical Co., Philadelphia, Pennsylvania.

Alamine 336 (impure tricaprylamine) is a tertiary amine, available from General Mills, Inc., Kankakee, Illinois.

Aliquat 336-S (impure tricaprylmethylammonium chloride) is a quarternary ammonium salt, available from General Mills.

Extractant solutions were made of the above high-molecular-weight amines by dissolving the appropriate quantities in xylene.

Cadmium-109 and zinc-65 tracers were obtained from the New England Nuclear Company, Boston, Massachusetts.

Aqueous standards (1000 ppm) for atomic absorption spectrophotometric analysis were obtained from Curtin-Matheson Company. The appropriate organometallic compound was purchased from Curtin-Matheson and dissolved in xylene for use as the standard for the nonaqueous phase analysis.

All of the aqueous solutions were prepared using deionized water.

Metal-Finishing Wastewater

The metal-finishing wastewater was obtained from the Dixie Metal Finishing Plant, Houston, Texas. It is a medium-sized plant which generates between 40,000 and 50,000 gal of wastewater a day. The plant is diversified, utilizing many metal-finishing procedures. The wastewater from the various processes after appropriate pH adjustments is combined to leave the plant at a single outlet and then treated by an ion-exchange system. Samples of the untreated wastewater were collected for investigation. They contained all of the metallic ions of interest: cadmium, chromium, copper, nickel, and zinc. Their composition varied widely depending on when the sample was taken. This apparently depended on the metal-finishing process which was taking place at the time of the sampling operation. Generally, the wastewater content was: chromium 12 to 60 ppm, cadmium 2 to 8 ppm, copper 0.5 to 5 ppm, zinc 2 to 14 ppm, and nickel 2.2 to 2.5 ppm, The pH usually ranged between 4 and 5. The water was somewhat turbid and a brown gelatinous sludge formed in the bottom of the vessel on settling.

RESULTS

Screening Studies

Screening studies were performed on synthetic solutions of cadmium, chromium, copper, nickel, and zinc using Primene JM-T, Primene 81-R, Amberlite LA-1, Alamine 336, and Aliquat 336-S as extractants. In a typical screening study, 5 ml of a 5% solution of the high-molecular-weight amine in xylene was placed in a 50-ml heavy wall centrifuge tube with an equal volume of 10 ppm metal ion solution. The phases were mixed for 3 min using a small motor stirrer equipped with a glass paddle. The phases were separated using a clinical centrifuge. After phase separation, each was analyzed for its metal content using an atomic absorption spectrophotometer. In some cases the cadmium and zinc were analyzed using a gamma scintillation counter with cadmium-109 and zinc-65 as tracers.

Extraction of Chromium

The screening studies indicated that Alamine 336 and Aliquat 336-S showed promise as satisfactory extractants for chromium. Generally, Alamine 336 was effective in acid media and Aliquat 336-S effective in slightly alkaline solution. Both removed more than 99% of the metal with a single extraction when carried out under optimum conditions. Alamine 336 was chosen for further investigations since the pH of the wastewater was usually between 4 and 5. In addition, raising the pH will cause some of the metals to precipitate out as the hydrous oxides and cause unwanted sludge.

Attempts were initially made to extract the chromium from the wastewater as received from the plants by vigorously shaking the water and analyzing rapidly. This proved unsuccessful due to the clogging of the aspiration system of the spectrophotometer and the frequent necessity for cleaning the burner head. Clogging problems were also encountered when the mother liquor from settled wastewater was used. Filtered wastewater samples were used in all subsequent investigations.

The pH was generally in the range of 4 to 5 when received from the plant. If the pH was higher than 5, it was lowered prior to filtration to prevent loss of the metals as hydrous oxides.

A high aqueous phase to organic phase ratio is desirable in order to concentrate the chromium into a small volume. Ratios up to 100 to 1 proved satisfactory. Higher ratios increased settling time due to formation of emulsions. The high aqueous to organic phase ratios caused a need for a higher Alamine 336 concentration than that used in the screening studies. The 5% Alamine 336 solution did remove the chromium efficiently with a single extraction, but on standing, the solutions turned green and the chromium content of the aqueous phase increased. This situation did not arise if a 25% reagent solution was used.

At a chloride ion concentration of 2×10^{-3} M (as hydrochloric acid) or higher, 90% of the chromium can be removed from the wastewater. The pH of the 2×10^{-3} M chloride solution varied from about 2.5 to 3.0 depending on the initial pH and composition of the samples. Some wastewater samples showed considerable buffering actions, presumably due to phosphates and/or borates used in the plating operations. Improving the extraction efficiency substantially above 90% was difficult. Increasing the Alamine 336 concentration or reducing the aqueous phase to organic phase ratio did not materially improve the degree of extraction. Carrying out a second extraction on the raffinate from the first extraction removed only 1 to 2% of the remaining chromium. It appears that only about 90% of the chromium is in the hexavalent state under the conditions of the extraction. The remaining 8 to 10% appears as trivalent chromium which cannot be extracted into the organic phase. In the screening studies in which K_2CrO_4 was used as the source of chromium, 99% of the chromium was removed under the same conditions. The chromium(III) was oxidized to chromium(VI) by acidifying the wastewater, adding potassium permanganate, and heating. On extracting the oxidized wastewater, more than 99% of the chromium was removed.

Further studies indicated that chromium can also be extracted selectively (about 90% of the chromium) by controlling the chloride ion concentration. At a chloride ion concentration of 2×10^{-3} M, no detectable quantities of cadmium, copper, nickel, or zinc are extracted when the extractions are carried out with 25% Alamine 336 in an aqueous to organic phase ratio of 100 to 1.

Extraction of Cadmium

Screening studies indicated that Primene JM-T, Alamine 336, and Aliquat 336-S can remove more than 95% of the cadmium from synthetic solutions with a single extraction. Of the three reagents, Alamine 336 appeared to be superior and was chosen for further investigations. If sufficient hydrochloric acid is added to the metal-finishing wastewater sample (after removing the chromium) to make the solution 0.03 *M* in chloride ions, more than 90% of the cadmium can be removed from the solution. This extraction is again carried out using 25% Alamine 336 and an aqueous phase to organic phase ratio of 100 to 1. Unfortunately, about 1% chromium and about 8% zinc are also extracted. No copper or nickel was extracted under these conditions.

Extraction of Zinc

If the wastewater raffinate after removal of both chromium and cadmium is further acidified with hydrochloric acid such that the chloride concentration is 0.4 *M*, approximately 85% of the zinc is removed from the solution. The extractions were again carried out using 25% Alamine 336-xylene solutions and an aqueous to organic phase ratio of 100 to 1. A single extraction was used as in the other studies.

Extraction of Copper and Nickel

In the screening phase of the study, copper and nickel showed some promise of being extracted with Aliquat 336-S. The extraction efficiencies were low except in alkaline solutions. No detectable quantities of copper or nickel were extracted with Alamine 336 under the optimum conditions described for chromium, cadmium, and zinc.

Selective Extraction of Chromium, Cadmium, and Zinc

In a typical laboratory extraction, the metal-finishing wastewater was filtered through a No. 1 fluted filter paper. To a liter of the filtered solution was added 5.0 ml of 0.4 *M* hydrochloric acid. A 25-ml sample of the wastewater was removed and analyzed for chromium, copper, cadmium, nickel, and zinc with an atomic absorption spectrophotometer. To the remaining solution was added 10.0 ml of 25% Alamine 336–xylene solution. The phases were then stirred in a 2-liter beaker for 3 min using a motor-driven stirrer. The resulting mixture was transferred to a liter separatory funnel and allowed to settle for 20 min. The phases were then separated. A 25-ml sample of the aqueous phase was analyzed for cadmium, chromium, copper, nickel, and zinc.

To the raffinate from the first extraction was added 25 ml of concentrated hydrochloric acid and 10.0 ml of 25% Alamine 336–xylene solution. The resulting mixture was again extracted and its raffinate analyzed for the five metals.

To the remaining raffinate from the second extraction was added 30 ml of concentrated hydrochloric acid and 10.0 ml of 25% Alamine 336–xylene solution. The resulting mixture was extracted and its raffinate analyzed for cadmium, chromium, copper, nickel, and zinc. The results from eight analyses are shown in Table 1. No copper or nickel was extracted in either of the extractions.

Simultaneous Extraction of Chromium, Cadmium, and Zinc

To a liter of the filtered metal-finishing wastewater was added 33 ml of concentrated hydrochloric acid. Twenty-five milliliters of the solution

TABLE 1

Selective Extraction of Chromium, Cadmium, and Zinc[a]

	Chromium		Cadmium		Zinc	
	Mean % extracted	*SD*	Mean % extracted	*SD*	Mean % extracted	*SD*
First extraction, 0.002 *M* chloride	88.6	4.0	0.0	0.0	0.0	0.0
Second extraction, 0.03 *M* chloride	0.65	1.09	94.1	1.65	8.1	2.1
Third extraction, 0.4 *M* chloride	0.55	0.87	4.8	1.3	80.9	3.5
Total metal extracted	89.8		98.9		89.0	

[a] Composition of wastewaters: Cr 10.0 to 56.8 ppm, Cd 4.1 to 5.9 ppm, Zn 5.2 to 9.2 ppm, Cu 0.3 to 0.5 ppm, and Ni 0.4 to 0.5 ppm.

TABLE 2

Simultaneous Extraction of Chromium, Cadmium, and Zinc[a]

	Chromium		Cadmium		Zinc	
	Mean % extracted	*SD*	Mean % extracted	*SD*	Mean % extracted	*SD*
First extraction	90.6	1.2	98.0	0.11	83.3	0.11
Second extraction	0	0	1.4	0.86	15.4	1.8
Total metal extracted	90.6		99.4		98.7	

[a] Composition of wastewaters: Cr 8.0 to 9.0 ppm, Cd 3.7 to 4.0 ppm, Zn 4.8 to 5.2 ppm, Cu 0.3 to 0.5 ppm, and Ni 0.4 to 0.5 ppm.

was removed and analyzed for chromium, cadmium, zinc, copper, and nickel. To the remaining solution was added 10.0 ml of 25% Alamine 336-xylene solution. The phases were mixed using a magnetic stirrer for 3 min. The mixture was then transferred to a 1-liter separatory funnel and allowed to settle for about 10 min. The phases were then separated and the aqueous phase again analyzed for the five metals.

To the raffinate from the first extraction was added another 10.0 ml of the 25% Alamine 336–xylene in order to carry out a second extraction. The results of the 10 analyses of the metal-finishing wastewater of varying composition are shown in Table 2. No copper or nickel was extracted in either extraction.

Reagent Loss

A study was carried out to determine if any Alamine 336–xylene solution would dissolve in the aqueous phase during the extraction processes. A Dorhmann Model DC-50 Total Organic Carbon Analyzer was used in the investigation. The total organic carbon (TOC) did increase during the extraction process. Generally, the TOC content increased approximately 50 ppm per extraction. The extractions were carried out using the usual 100 to 1 aqueous to organic phase ratio and 25% Alamine 336–xylene solution.

Stripping and Recycling

After extracting the toxic metal ions from the metal-finishing wastewater into the organic phase, it is desirable to recover the metals, thus regenerating the Alamine 336–xylene solvent in order that it may be recycled.

TABLE 3

Stripping Studies[a]

	Mean % stripped	*SD*
1. Chromium	99.86	0.10
2. Cadmium	99.53	0.18
3. Zinc	99.95	0.03

[a]Stripping solution: Cr 3 to 5 mg/ml, Cd 0.6 to 0.8 mg/ml, and Zn 1 to 1.5 mg/ml. Strippant: 4.0 *M* NaOH.

This process, generally called stripping, is very important in developing an economic cyclic industrial process. A series of strippants was investigated including sulfuric acid, ethylenediamine, EDTA, and sodium hydroxide. Of these, sodium hydroxide proved to be most effective.

In a typical stripping experiment, to 10 ml of the organic phase (Alamine 336-xylene) containing 3 to 5 mg/ml chromium, 0.6 to 0.8 mg/ml cadmium, and 1.0 to 1.5 mg/ml zinc is added 3.0 ml of 4.0 *M* sodium hydroxide solution. The phases are mixed for 3 min in a 50-ml beaker using a magnetic stirrer. The mixture is allowed to settle for 15 min for phase separation. The organic phase was then analyzed for chromium, cadmium, and zinc. Stripping studies were carried out on ten solutions. The results (Table 3) show that more than 99.5% of the chromium, cadmium, and zinc were removed from the organic phase in a single stripping operation.

The regenerated Alamine 336–xylene solution was used again to extract the metals from the wastewater without loss of any efficiency. Fifteen cycles were carried out using the same solvent without loss of efficiency. No larger number of cycles was investigated.

DISCUSSION

The mechanism for the extraction of cadmium and zinc from the metal finishing wastewater is:

$$M^{2+} + 4Cl^- \rightleftarrows MCl_4^{2-}$$

$$2[R_3N]_o + 2H_a^+ + [MCl_4]_a^{2-} \rightleftarrows [[R_3NH]_2MCl_4]_o$$

The mechanism for removing the chromium is:

$$2[R_3N]_o + 2H_a^+ + [Cr_2O_7]_a^{2-} \rightleftarrows [[R_3NH]_2Cr_2O_7]_o$$

where R_3N = Alamine 336

M = Cd or Zn
o = organic phase
a = aqueous phase

The complexes formed by cadmium, zinc, and chromium with Alamine 336 are soluble in common organic solvents such as xylene, benzene, and kerosene.

The extraction parameters associated with the selective extraction of chromium, cadmium, and zinc are somewhat critical. Chromium can generally be removed without contamination by cadmium and zinc. The chromium could be reclaimed and returned to the plating bath. There were some metal-finishing samples in which each of the three metals could be extracted selectively without any contamination of the other two metals. A general procedure with industrial potential appears unlikely for the selective extraction of cadmium and zinc due to the great variation in wastewater.

The simultaneous extraction of all three metals appears promising if a second extraction is carried out.

The metals can be easily stripped quantitatively from the Alamine 336–xylene with 4 *M* NaOH. The amine solvent can be regenerated and reused repeatedly, making the process attractive for industrial utilization.

The reaction mechanisms for stripping with sodium hydroxide are as follows:

$$[[R_3NH]_2Cr_2O_7]_o + 4OH^- \rightarrow 2[R_3N]_o + 2[CrO_4]_a^{2-} + 3H_2O$$

$$[[R_3NH]_2CdCl_4]_o + 4OH^- \rightarrow 2[R_3N]_o + Cd(OH)_2\downarrow + 4Cl^- + 2H_2O$$

$$[[R_3NH]_2ZnCl_4]_o + 6OH^- \rightarrow 2[R_3N]_o + [Zn(OH)_4]_a^{2-} + 4Cl^- + 2H_2O$$

The procedures discussed here merit further study. Pilot plant studies should be carried out on the processes, particularly the simultaneous extraction method. It shows promise for utilization by small metal-finishing plants.

Acknowledgments

The authors wish to thank Mr. Frank Rudman of the Dixie Metal Finishing Company for supplying them the wastewater. They also wish to thank Ms. Orbie S. Cowling, Mr. Ta-Sheng Lin, Mr. Mohammed Mahayni, and Mr. Hossein Pahlavan for their technical assistance. Special appreciation goes to Industrial Waste Treatment Research

Laboratory of the Environmental Protection Agency, particularly Mr. J. Ciancia, Mr. R. Tabakin, and Ms. M. Stinson, who monitored the project, and the MIRS branch of EPA which financed the research.

REFERENCES

1. R. Pribil and V. Vesley, *Collect. Czech. Chem. Commun.*, *37*, 13 (1972).
2. H. Mahlman et al., *Anal. Chem.*, *26*, 1939 (1954).
3. A. K. Reed et al., *Research Report 56*, *Batelle Memorial Institute*, July 1970.
4. F. Seeley and D. Crouse, *J. Chem. Eng. Data*, *11*, 424 (1966).
5. T. Florence and J. Farrar, *Anal. Chem.*, *40*, 1200 (1968).
6. C. W. McDonald and F. L. Moore, *Ibid.*, *45*, 983 (1973).
7. F. L. Moore, *Sep. Sci.*, *7*, 505 (1972).
8. C. W. McDonald and T. Rhodes, *Anal. Chem.*, *46*, 300 (1974).
9. C. W. McDonald and T. Rhodes, *Sep. Sci.*, *9*, 441 (1974).
10. C. W. McDonald and T. Lin, *Ibid.*, *10*, 499 (1975).
11. F. L. Moore, *Ibid.*, *10*, 489 (1975).
12. F. L. Moore, *Environ. Lett.*, *10*, 37 (1975).
13. H. Reinhardt, *Chem. Ind.*, *1975*, 200 (March).

Received by editor September 24, 1976