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Separation and Concentration of Metals Present in Industrial Effluent and Sludge Samples by Using Electrodialysis, Coulometry, and Photocatalysis

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ABSTRACT

Samples of effluent and sludge collected from the metal plating industry were treated by electrodialysis (ED), coulometry, and photocatalysis. The effects of different ED parameters (such as flow rate, applied voltage and current) and the single pass and recirculation methods on the percentage reduction of ionic components of an effluent sample and the percentage concentration of metal ions in the sludge solution have been determined. A maximum of 40–60% reduction in the composition of effluent sample and about 39–47% concentration of metal ions in sludge solution have been obtained. The recirculation method for the concentration of metal ions at a high flow rate of sludge solution seems to be better than the single pass method at low flow rates. Copper, which is a valuable component in sludge samples, has been recovered by constant potential electrolysis with a coulombic efficiency of 90–97% and has also been deposited to 57–76% on a colloidal suspension of TiO_2 particles using UV and natural sunlight. The effects of treatment of TiO_2 with H_2 at 400°C and the nature of a sacrificial electron donor in contact to TiO_2 on the photodeposition of copper are discussed.

INTRODUCTION

Various precious and common metals enter into water through washing, rinsing, pickling, and other surface treatment procedures adopted in indus-

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tries such as hydrometallurgy, plating, and photography. Metals in effluents, sludges, and other industrial wastes not only represent significant losses in raw material but are also of major concern as environmental pollutants. Therefore, the development of techniques to recover/reuse the metals from wastes or to treat industrial effluents is of immense technology value.

Conventional methods to remove metals from effluents are based on chemical precipitation, absorption on charcoal, ion exchange, and encapsulation/chelation (1). These methods have certain disadvantages, viz. 1) the need to use enormous amounts of chemicals, resins, and supports whose regeneration is very cumbersome and sometimes uneconomical, and 2) the nonselectivity for metal ions which leads to a mixture of metal-ion-containing products. Modern methods include membrane processes such as reverse osmosis and electrodialysis (ED). They have been developed primarily for the desalination of saline water, but also find application for the treatment of industrial effluents (2, 3). The electrodialysis technique is employed for the separation of electrolytes present in effluents. Its application to treat effluents from the electroplating (2) (nickel, copper, etc.) industry has been reported (3). As electrodialysis helps to concentrate the metal in the effluent, it would be possible to raise the metal ion concentration level in the effluent to match that of the actual bath concentration and thus permit reuse of the concentrate in plating/deposition baths. Metals of high purity can be recovered by constant potential/current coulometry (electrowinning) (4). As the metal deposition is specific to the applied potential, selective deposition of a particular metal in high purity from effluents of a mixed metal ion character can be achieved. An interesting new application of heterogeneous photocatalysis to recover various metals from waste is becoming attractive (5–8). In this method various illuminated semiconductors have been used for the photodeposition of metals (semiconductor surface metallation) such as Au, Ag, Pt, Pd, Rh, Hg, Pb, and Co from aqueous solutions (8–12) along with the couples Pt–Rh, Ag–Rh, and Pt–Pd (13). The photodeposition of most metals involves the reduction of metal ions by conduction band electrons and the oxidation of water or any sacrificial electron donor by valence band holes. Obviously, only those metal ion species with reduction potentials more positive than the conduction band edge can be photodeposited. For the most popularly used photocatalyst, titanium dioxide (TiO_2), the positions of conduction and valence band edges (at pH 0) are -0.2 and $+3.0$ eV (versus NHE), respectively.

In the present study the techniques of electrodialysis, coulometric deposition, and photocatalysis have been applied to separate/concentrate metals (Cu, Fe, and Zn) from a precharacterized effluent and sludge connected with the plating industry. This study has been made to explore the feasibility of applying these techniques to treat effluents and sludges of a mixed metal ion character. We note here that as the underlying working principles of these techniques differ widely, an absolute comparison of their performances for separation/concentration is omitted. Under various chosen conditions, the percentage concentrations for Cu, Fe, and Zn varied between 40 and 50% using ED (both in single pass and recirculation conditions), constant potential coulometric deposition of copper occurred with 90–97% coulombic efficiency, and a maximum of 80% copper could be recovered photocatalytically as a deposit on titania photocatalyst.

EXPERIMENTAL SECTION

Effluent and sludge samples were collected from a metal plating industry. The effluent was used as received, while a solution of the sludge to use in these studies was prepared as follows: 1.5 kg of powdered sludge was dissolved in 2 L concentrated HCl (2, 3). This acid solution, after complete neutralization of the carbonates, was filtered and diluted to 20 L. The analytical data pertinent to these samples are summarized in Table 1.

The description and function of the electrodialysis (ED) unit, which contained 20 cells pairs, each of 0.16 cm thickness, of alternatively arranged cation and anion-exchange interpolymer membranes having a crossflow arrangement, was described earlier (14). Cation and anion membranes of 80 cm^2 cross-section were prepared by a method developed in our laboratory (15). The aerial resistances of these membranes were measured to be around 1–2 ohm·cm^2 for cation and 3–5 ohm·cm^2 for anion membranes.

TABLE 1

Analytical Data of the Original Effluent (pH 7.9), Sludge, and Sludge Solution (pH 0.8)

Constituent	Effluent (ppm)	Sludge (in kg per kg)	Sludge solution (ppm)
Residue	—	0.243	—
TDS[a]	1,630	0.747	43,465
Cl^-	107	—	39,050
Cu	120	0.028	2,133
Zn	197	0.002	146
Fe	—	0.003	230

[a] Total dissolved solids.

Anodic stripping differential pulse voltammetry (ASDPV) for estimating copper and zinc, and differential pulse polarography (dpp) for estimating iron were carried out on an EG&G PAR model 174A, polarographic Analyzer coupled to a high precision X-Y recorder and a three-electrode assembly (16). A mercury drop (dme or HMDE) with a 0.017 cm^2 surface working area, an SCE as reference, and a Pt wire as auxiliary electrode were used for this purpose.

Treatment of Effluent Sample by ED

A known volume of the effluent was taken in two aspirator bottles of 10 L capacity, marked as the diluate (T) and the concentrate (C), with an outlet arrangement. These bottles were elevated so the effluent would flow under gravity. The outlets of T and C were connected to the inlets of an ED unit so the solutions in T and C would pass through alternate compartments. After adjusting the flow rates to the desired value, a dc voltage (30–40 V) at constant current (between 35 and 50 mA) was applied. For a given set of experimental condition (voltage, current, and flow rate), the diluate stream coming from the ED unit, considered as a single pass, was collected for 30 minutes and analyzed. The reductions percentage in TDS, Cl^-, Cu, Zn, and Fe were estimated.

Concentration of Sludge Solution by ED

Single Pass

A known volume of sludge solution was taken in T and C, and each was allowed to flow simultaneously through alternate compartments of the ED stack. After adjusting the flow rates to 2.5 L·h^{-1} diluted and 0.6 L·h^{-1} concentrate, a constant dc voltage (30 V) at a current density of 3.125 mA·cm^{-2} was applied. The diluate and concentrate streams, identified as T_1 and C_1, were collected at the outlets of the stack and analyzed. Finally, the percentage reductions in T_1 and the percentage concentrations in C_1 of TDS, Cl^-, Cu, Zn, and Fe were calculated.

Recirculation Method

In this method the sludge solutions (7 L in bottle T and 4 L in bottle C) were passed at the flow rates of 21 L·h^{-1} diluate and 10.8 L·h^{-1} concentrate through an ED unit at 35 V. The diluate and the concentrate streams collected at the outlets of the ED unit were then pumped to their respective bottles for recirculation. The dilute (T_2) and concentrate (C_2) solutions thus obtained after 2 hours of recirculation were analyzed. The current density varied from 3.1 to 1.1 mA·cm^{-2} during the whole operation.

Estimation of Copper and Zinc

A mixture of 5 mL of 0.2 M ammonium citrate (pH 3), 5 mL effluent or 10 mL of 0.1 M ammonium citrate (pH 3), and 5 mL sludge solution containing 0.1 mL of 10% hydroxylammonium chloride was warmed to 70°C for 15 minutes. It was then cooled, deaerated with Ar, and ASDPV was run from -1.2 V at HMDE under static conditions. The deposition procedure included deposition for 30 seconds under stirring and 30 seconds under nonstirring conditions by holding the HMDE at -1.2 V. The peak currents at -1.05 V for Zn(0)/Zn(II) and -0.06 V for Cu(0)/Cu(II) were compared with those of standard samples, and the Cu or Zn content was calculated.

Estimation of Iron

To a mixture of 5 mL of 0.5 M triethanolamine and 0.4 M NaOH, 5 mL effluent (or 0.5 mL sludge solution in 5 mL distilled water) was added. The mixture was filtered, warmed for 10 minutes, and dpp was run under Ar. The peak height of Fe(III)/Fe(II) at -1.0 V was measured and compared with that of a standard solution to obtain the concentration of iron in the test solution.

Coulometric Deposition of Copper

Copper in a 20-mL sludge solution (before or after ED treatment) was deposited on a copper electrode (38.7 cm^2) by constant potential (-0.4 V versus SCE) coulometry. Cu was also deposited from a solution prepared by dissolving 1 g sludge in 2 mL of concentrated H_2SO_4 which was diluted to 20 mL.

Photocatalytic Deposition of Copper on TiO_2 Particles

Titanium dioxide (Aldrich Co., mean particle diameter < 0.2 μm) was used as received or after treatment in H_2 gas at 400°C for 8 hours. These experiments generally involved the exposure of 1 g TiO_2 suspension with or without a sacrificial electron donor in 20 mL sludge solution to UV light from a 400-W Hg lamp or natural sunlight under stirring. HCOOH (5 mL), Na_2EDTA (1 g), and CH_3COOH (5 mL) were used as sacrificial electron donors. At the end of the experiment each of these solutions was filtered, treated with 5 mL concentrated HNO_3 and 5 mL of 60% $HClO_4$, and then slowly evaporated. The residue was dissolved in a minimum volume of water, filtered, and diluted to 25 mL. This solution was then analyzed for copper content by ASDPV as described above.

RESULTS AND DISCUSSION

The data given in Table 1 show that 1 kg of the original sludge contained 28 g copper, which was greater by 9 and 14 times that of iron and zinc, respectively. The effluent, on the other hand, had 120 ppm copper, 197 ppm zinc, and undetectable amounts of iron. It appears that the method of pretreatment of effluent adopted by the concerned metal plating industry might have resulted in a profound accumulation of copper, iron, and zinc into the sludge.

Effluent Treatment by ED

The effects of various ED parameters on the percentage reduction in the concentrations of TDS, Cl^-, Cu, Zn, and Fe of the effluent sample are shown in Table 2. From Set 1 it can be seen that at flow rates of 3.6 $L \cdot h^{-1}$ diluate and 1.2 $L \cdot h^{-1}$ concentrate solutions, the percentage reduction of ionic components in the effluent sample gradually increased with increases in the applied voltage and current. These flow rates and the applied voltage (40 V) and current (50 mA) give a maximum percentage reduction of TDS, Cl^-, and metal ions between 40 and 60%. This percentage falls when the flow rate of either the diluate, the concentrate, or of both solutions (see Sets 2 and 3) were increased under the optimized conditions of ED voltage and current.

TABLE 2
Effect of ED Parameters on Percentage Reduction of TDS, Cl^-, and Metal Ions Composition in Effluent Sample

Set	Flow rate ($L \cdot h^{-1}$) T	Flow rate ($L \cdot h^{-1}$) C	Voltage (V)	Current (mA)	Final pH	Percentage reduction Cl^-	TDS	Cu	Zn
1	3.6	1.2	30	40	5.7	40	20	25	25
			35	45	5.4	53	40	40	39
			40	50	5.3	60	41	43	45
2	7.2	1.8	30	35	6.8	21	12	13	17
			35	40	6.4	34	15	18	21
			40	45	5.9	34	20	21	24
3	12.5	3.0	40	50	7.2	27	10	11	14

Concentration of Sludge Solution by ED

The analytical data corresponding to a sludge sample after ED treatment in the single pass and recirculation methods are given in Table 3. In the single pass method, the percentage of reduction of TDS, Cl^-, and metal ions was between 11 to 13 in the diluate stream (T_1). The percentage of reduction was enhanced to 17–21% by the recirculation method even at a high flow rate. This percentage concentration of was nearly four times higher in the case of the single pass method and double in the recirculation method than the corresponding percentage reduction in diluate streams (T_1 and T_2). These differences are accounted for the differences in the volumes of diluate and concentrate solutions with which the experiments were carried out and their flow rates. In general, for a high TDS solution, the recirculation method is preferable in ED. The data in Table 3 also reflect that the percentage reduction in metals recovery from sludge solution was not as much as expected. One reason for the poor performance of the ED unit may be the high trivalent iron content (205 ppm) in the sludge solution. It was found that the recirculation method was more suitable for metal ion recovery from solutions of high TDS.

Separation of Copper from Sludge Sample

As the sludge sample contained considerably more copper than other metal ions and our main interest was to separate the copper, we further used the constant potential coulometric and photocatalytic methods to deposit copper in its elemental form. The relevant data are presented in

TABLE 3

Analytical Data after ED Treatment of Sludge Solution (pH 0.8) Under Single Pass (T_1, C_1) and Recirculation (T_2, C_2) Methods[a]

Set	Flow rate ($L \cdot h^{-1}$)	Voltage (V)	Current ($mA \cdot cm^{-2}$)	Final pH	Cl^- (ppm)	TDS (ppm)	Cu (ppm)	Zn (ppm)	Fe (ppm)
T_1	2.5	30	3.125	0.78	34.952 (11)	38.250 (12)	1.897 (11)	127 (13)	205 (11)
C_1	0.6	30	3.125	0.72	54.670 (40)	61.720 (42)	3.075 (44)	215 (47)	320 (39)
T_2	21.0	35	3.1–1.1	0.75	32.000 (18)	36.090 (17)	1.723 (19)	115 (21)	184 (20)
C_2	10.8	35	3.1–1.1	0.66	51.540 (32)	56.500 (30)	2.900 (36)	204 (40)	320 (39)

[a] Values given in parentheses refer to percentages.

TABLE 4

Constant Potential Coulometric Deposition of Copper from Oxygen-Excluded Sludge Sample. Cathode (Cu) Area = 38.7 cm^2; Applied Potential = −0.4 V vs SCE at 25°C

Sludge taken	Weight gained by cathode (g)	No. of coulombs consumed	Coulombic efficiency
20 ml solution	0.040	126	95.2
20 ml solution	0.063	192	96.7
1 g sample[a]	0.025	84	90.4

[a] Sludge was disolved in 2 mL of conc. H_2SO_4 and then diluted to 20 mL.

Tables 4 and 5. The complete deposition of copper was achieved coulometrically with 90–97% coulombic efficiency. In the photocatalytic method (Table 5), a minimum of 2 hours exposure of UV light or 6 hours' exposure to natural sunlight is required to achieve near-saturation deposition of copper in TiO_2. The copper concentration in the original sludge solution, in the case of the best suited system, goes from 2133 ppm to approximately 425 ppm. This represents 80% removal of copper from the industrial sludge. Examination of Table 5 shows that 1) the as-procured untreated catalyst is the most active; 2) copper deposition is faster under UV light; 3) the presence of sacrificial electron donors has a marginal increasing influence on photodeposition (e.g., HCOOH) or actually lowers the extent

TABLE 5

Effect of Treatment of Catalyst Addition of Sacrificial Electron Donor, and Source of Light on the Percent Deposition of Copper on the Titania Catalyst from the Sludge Solution (0.043 g/L of Cu^{2+})

		% Copper deposition	
Photocatalyst (1 g)	Sacrificial electron donor (g or mL)	UV (1 hour)	Sunlight (6 hours)
Treated	—	65.3 79.9[a]	75.7
	HCOOH	73.4	68.8
	EDTA	63.2	56.6
	CH_3COOH	60.2	56.6
Untreated	CH_3COOH	45.1	14.9

[a] Two hours

of deposition by strong complexation to Cu^{2+} ions, as would be the case with CH_3COOH or EDTA; and 4) the added sacrificial electron donors (in the case of treated TiO_2 catalyst, both in UV and natural sunlight) exhibit an increase in reactivity in the order HCOOH > EDTA > CH_3COOH.

Reiche et al. (17), as early as 1979, studied the complete reduction of copper ion to metallic copper at TiO_2 in aqueous solution in the presence and absence of acetate ion. Bideau et al. (18) observed the formation of red Cu–TiO_2 when solutions containing copper ion and formate were irradiated in the presence of TiO_2. Fostu et al. (19) recently demonstrated the potential utility of the TiO_2 photocatalytic process for the treatment of waste streams containing copper and various organic species where the percentage recovery of copper was 90. The data presented in this paper also suggest the feasibility of removing copper from sludge by heterogeneous photocatalysis as directly applied to an industrial sludge of mixed metals for the first time. The copper-deposited TiO_2 may be used as a catalyst or the copper may be recovered via oxidative dissolution of copper on Cu/TiO_2 in a HNO_3–H_2O_2 mixture.

CONCLUSIONS

Treatment of industrial effluent and recovery of valuable metals for reuse from industrial wastes by physicochemical methods are of current research interest. In the present research we reduced the ionic composition of effluent to 41–60% by ED single pass at a flow rate of 3.6 $L \cdot h^{-1}$ diluate under an applied voltage of 40 V and a current of 50 mA. We concentrated the metal ions of copper, zinc, and iron present in a sludge solution (TDS = 43,465 ppm, pH 0.8) to 49, 47, and 39%, respectively, by ED. Constant potential electrolysis and photocatalytic methods have been used to recover the copper present in a sludge sample. Copper was completely recovered by the former method. In the photodeposition method, about 65 and 76% copper was obtained when a colloidal suspension of treated TiO_2 and the sludge solution were exposed to UV (1 hour) and sunlight (6 hours), respectively. The percentages were reduced to 69–73 under UV light and 57–69 under sunlight when complexing carboxylic acids were added as sacrificial electron donors.

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