

# Electrochemical Oxidation of Cyanide and Simultaneous Cathodic Removal of Cadmium Present in the Plating Rinse Water

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The electrochemical oxidation of cyanide, with the simultaneous recovery of cadmium present in a typical plating rinse wastewater, was conducted in a bipolar capillary gap disc stack electrochemical reactor under batch recirculation mode. The concentrations of cyanide and cadmium present in the reservoir of the batch recirculation system were measured as a function of electrolysis time at various flow rates, pH values, and applied cell potentials. The objective of this work was to explore the feasibility of using a bipolar disc electrochemical reactor that consisted of graphite as the electrodes to remove cyanide and Cd ions from the plating industry effluent using batch continuous recirculation modes. Experimental results showed that the reactor was able to reduce (from rinse water with a cyanide concentration of 240 mg/L and cadmium concentration of 50 mg/L) the content of toxic species by more than 99%, so that the treated water can be reused for further operations.

## 1. Introduction

Metal-plating industries generate large volumes of wastewater from spent rinses that contain toxic metal ions such as Cd, Cu, Au, Pb, Ni, Ag, and Zn ions, as well as acids, alkalis, and cyanide. Therefore, the toxic and hazardous effluents that emanate from the plating factories must be properly treated, so that they do not cause more damage to the environment.<sup>1,2</sup> All these substances are highly toxic and have been regulated by the Pollution Control Board. In conventional treatments, the cyanide-bearing plating effluent is treated with alkaline chlorination, with the precipitation of metal ions as hydroxides, and it is being discharged into the public sewer. Water is a scarce resource. Government has stressed industry to increase process water recycling to reduce water consumption.

Cadmium is highly toxic;<sup>3</sup> it causes cancer, and it is teratogenic and potentially mutation-causing, with severe sublethal and lethal effects at low environmental concentration. It is associated with increased mortality, and it affects respiratory functions, enzyme levels, muscle contractions, growth reduction, reproduction, and bio accumulations in the livers and kidneys. The free cyanides inhibit cytochrome oxidase, thereby suppressing aerobic respiration and thus cause cyanide toxicity.<sup>4</sup> The toxicity of complex cyanides is usually low; however, the degradation products often include free cyanides, which are toxic.

There are several known methods for treating cyanide-bearing effluents from plating industries. Cyanide can be removed using chemical,<sup>5–8</sup> photolytic,<sup>9–11</sup> catalytic,<sup>12</sup> ultrasonic,<sup>13,14</sup> biological,<sup>15</sup> ion exchange,<sup>16</sup> and electrolytic methods.<sup>17–23</sup> The conventional means for treating wastewaters that contain cadmium follow alkaline precipitation. The methods frequently used for the removal of cadmium from solutions include chemical precipitation as a hydroxide, sulfide or as insoluble salts (combined with flocculation). This process presents a difficult task, with respect to the removal of the generated

sludge. Attempts have been made to avoid the expensive filtration that is required by this technique. Other methods such as adsorption,<sup>24,25</sup> ion flotation,<sup>26</sup> and electrocoagulation<sup>27</sup> have been shown to be applicable for removing metal ions from waste solutions. Unfortunately, all of these techniques, including chemical precipitation, are inappropriate for large solution volumes with very low concentrations of metal ions.

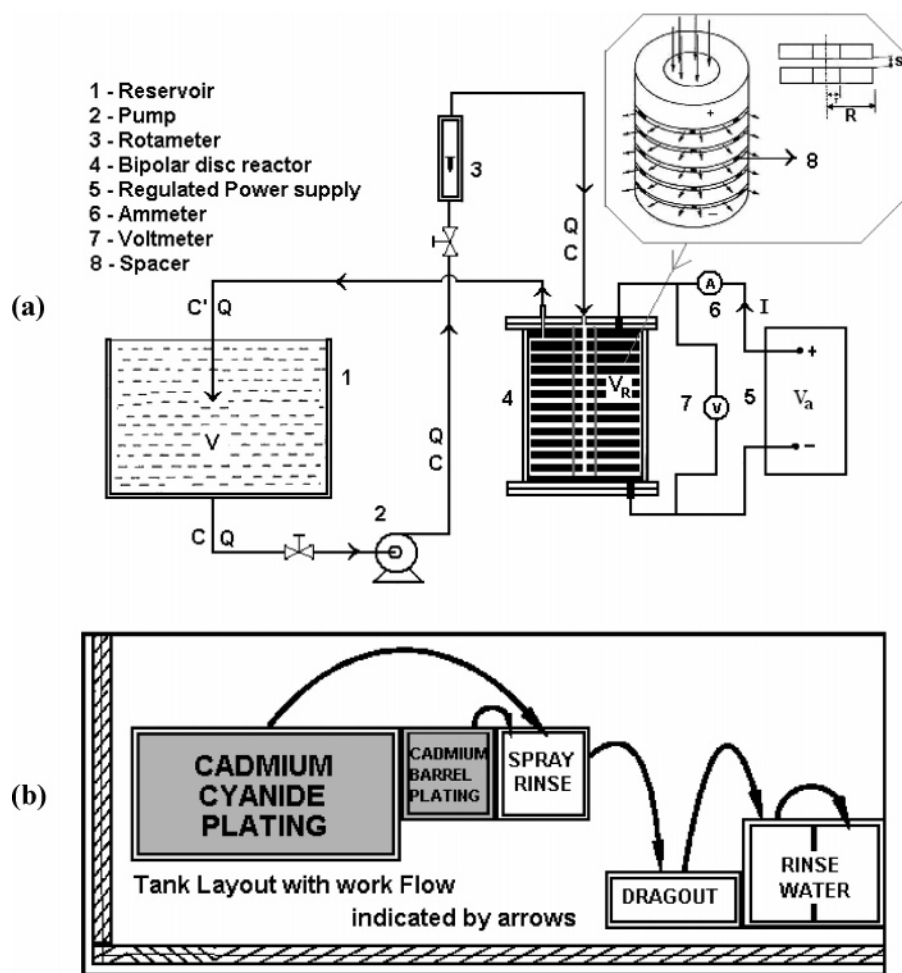
The electrochemical treatment method is an alternative process that generates no secondary pollutants.<sup>28</sup> In fact, the main reagent is the electron, which is a clean reagent. As a consequence, the electrochemical technique has been tested for several applications, such as metal ion removal and recovery,<sup>28,29</sup> as well as electrodialysis.<sup>30–32</sup> The electrochemical method is an alternative treatment technique for the destruction of cyanide at the anode and the recovery of heavy metals at the cathode without generating a sludge problem. Complex cyanide and concentrated cyanide solutions can also be treated using this method. The process is especially suitable for the electroplating industry, where the DC power supply is available and other plating equipment can be adopted for the waste treatment process. The destruction of cyanide and the simultaneous removal of cadmium present in the rinse water in an electrochemical process is achieved by direct or indirect anodic oxidation of cyanide, as well as by the cathodic reduction of cadmium directly at the cathode. The process of utilizing strong oxidizing agents, such as hypochlorite and chlorine that is generated during the electrolysis for the oxidation of pollutants, is called indirect oxidation.<sup>28</sup>

In the present investigation, the required amount of sodium chloride is added to the rinse water, which acts as a supporting electrolyte,<sup>33,34</sup> and in-situ-generated strong oxidizing agents such as hypochlorite and chlorine during the process treatment can be effectively utilized. Although many papers were published on the treatment of cyanide- and cadmium-containing rinse water, the use of bipolar disc stack reactors for treatment was not given much importance. Bipolar disc stack reactors have great interest, because of their simple geometry (see Figure 1a). The radially divergent flow in gaps will greatly enhance the rate of electrochemical reaction for low-conducting fluids. Bipolar disc reactors are widely preferred for electrochemical reactions, because of their compactness, and they are simple

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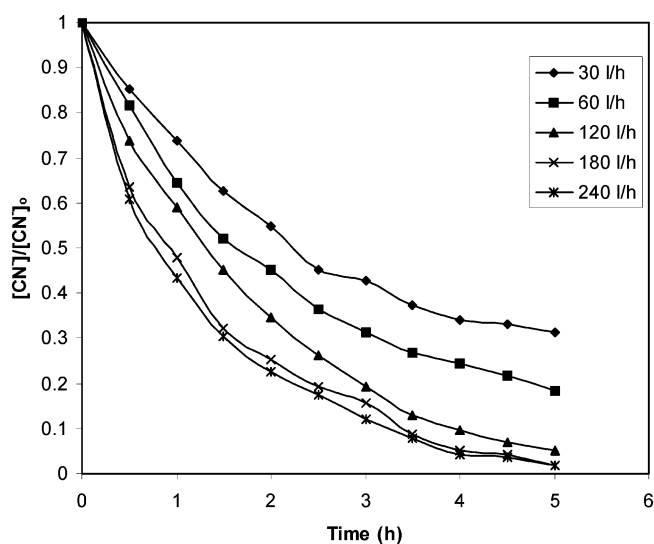
**Figure 1.** Schematic diagrams of (a) the experimental setup, with a perspective view of the bipolar stack reactor, and (b) the cadmium cyanide plating rinse tank layout, with the work flow indicated by arrows.

and easy to operate and maintain. The main disadvantage of this reactor is the presence of parasitic electrical currents or bypass currents through the electrolyte at the inlet and outlet of the electrode stack.<sup>35</sup> The electrochemical approach for the destruction of the cyanide ion and the cathodic removal of the Cd ion are not new; however, the effect of the paired task in this type of reactor that has been used is hitherto unknown. Again, the reactor is highly useful for handling low-conductivity rinse water, because a narrow-gap interelectrode distance can be maintained to the desired level to reduce the IR drop.

Hence, the main objective of the present work is to investigate the applicability of the electrochemical destruction of cyanide present in the effluent with a simultaneous removal of cadmium, using a bipolar disc stack reactor, so that the treated water can be reused for further operation.

## 2. Materials and Methods

**2.1. Materials.** All the chemicals used were of analytical grade. Based on the practical data collected from different plating industries (see Figure 1b for rinse water generation in industry), the synthetic rinse water concentration for the cyanide ion and the Cd ion was fixed at  $\sim 250 \pm 20$  mg/L of cyanide and  $\sim 50 \pm 5$  mg/L, respectively. The synthetic rinse water was prepared by dissolving the required amounts of sodium cyanide and cadmium chloride in a 200 mg/L sodium chloride supporting electrolyte solution. The pH of the electrolyte was maintained constant with the addition of 10 N sodium hydroxide solution.



**Figure 2.** Effect of the flow rates on the variation of the extent of unconverted cyanide ion with electrolysis time. Conditions:  $[CN^-]_0 = 240$  mg/L;  $[Cd^{2+}]_0 = 50$  mg/L; pH 10;  $[NaCl] = 200$  mg/L; applied potential = 40 V.

**2.2. Experimental Setup.** The schematic diagram of the experimental setup is shown in Figure 1a, with a perspective view of the disc stack system. The setup consists of a reservoir, a magnetically driven self-priming centrifugal pump, a flow meter and the electrolytic cell connected to an electrical circuit

**Table 1. Summary of the Results Obtained in the Oxidation of Cyanide and the Simultaneous Reduction of Cadmium<sup>a</sup>**

flow rate, $Q$ (L/h)	current, $I$ (A)	final $[\text{CN}^-]$ (mg/L)	final $[\text{Cd}^{2+}]$ (mg/L)	Power Consumption (kWh/kg)		Transfer Coefficient, $k^b$ ( $\times 10^4$ cm/s)	
				cyanide	cadmium	cyanide	cadmium
30	1.1	75	9	441.21	1775.60	4.1	5.5
60	1.2	44	7	433.69	1875.96	5.1	7.1
120	1.3	21	4	399.22	1899.99	7.3	9.1
180	1.4	4	1	393.22	1893.87	8.8	10.1
240	1.4	4	1	393.22	1893.87	9.9	10.4

<sup>a</sup> Reservoir volume,  $V = 3$  L; pH 10; applied voltage,  $\mathcal{V}_a = 40$  V; duration of electrolysis,  $t = 5$  h; electrode area,  $A_e = 636$  cm<sup>2</sup>;  $[\text{NaCl}] = 200$  mg/L;  $[\text{CN}^-]_0 = 240$  mg/L;  $[\text{Cd}^{2+}]_0 = 50$  mg/L. <sup>b</sup> For  $\text{CN}^-$  oxidation,  $k = 8.36u^{0.44}$  ( $R^2 = 0.99276$ ), and for  $\text{Cd}^{2+}$  reduction,  $k_L = 9.66u^{0.32}$  ( $R^2 = 0.98368$ ) (where  $R^2$  represents the coefficient of correlation).

consisting of a 3 A/120 V (DC) regulated power supply, an ammeter, and a voltmeter. The electrolytic cell is made of Perspex that contained 11 graphite disc electrodes. The cell stack consists of two circular polyvinyl chloride (PVC) end frames 1.25 cm thick. A hollow cylindrical Perspex rigid tube with an inner diameter of 10 cm and height of 11 cm is placed between these two frames. The two graphite discs were fixed onto the two PVC end frames. These two discs act as feeder electrodes, and the remaining nine discs are arranged between these two discs. The inner radius ( $r$ ) and outer radius ( $R$ ) of the disc are 0.5 and 4.5 cm, respectively. The spacers ( $s$ ), which are comprised of 4-mm-thick polypropylene bits, isolate the electrodes from each other (see Figure 1). A feeder electrode at the top acts as the anode and the bottom electrode acts as the cathode. In this way, the reactor acts as a stack of 10 unit cells fed into the solution in a parallel manner, maintaining the current series and flow parallel configuration system. The stack of circular disc electrodes has a 1-cm central bore, through which the electrolyte flows inward and the overflow was collected in the reservoir from the top of the reactor and continuously recirculated. Provisions have been made for the electrolyte inlet and outlet. The total cell volume without electrodes is  $\sim 780$  mL and with electrodes is  $\sim 370$  mL. The free volume of the electrolyzer is 400 mL, and the reservoir capacity is 3.0 L. The area of each disc is 0.636 dm<sup>2</sup>. Thus, the total area of anode/cathode for 10 unit cells is 6.36 dm<sup>2</sup>.

**2.3. Experimental Procedure.** Electrolysis was conducted under batch continuous recirculation mode. Total volume of 3 L of solution (rinse water that had a  $\text{CN}^-$  concentration of 240 mg/L and a  $\text{Cd}^{2+}$  concentration of 50 mg/L, with a supporting electrolyte concentration of 200 mg/L at pH 10) was taken for each experiment and circulated at the flow rate of 180 L/h through the reactor, and the applied voltage was 40 V for electrolysis. The extent of cyanide destruction, as well as the extent of cadmium removal, was studied under various conditions such as different cell voltages, pH values, and volumetric flow rates. The effluent was treated at two different cell voltages (viz., 30 and 40 V) and the pH was varied as pH 7 and pH 10. The liquid flow rate into the reactor was varied over a range of 30–240 L/h in five steps—namely, 30, 60, 120, 160, and 240 L/h. The flow rate of the effluent was measured using a calibrated rotameter, and the duration of the electrolysis was 5 h. The samples were drawn from the reservoir every half hour to estimate the cyanide and cadmium concentrations present in the electrolyte solution. The cyanide concentration was estimated using potentiometric titration,<sup>36</sup> whereas the cadmium concentration was estimated using atomic absorption spectroscopy (AAS).

### 3. Results and Discussion

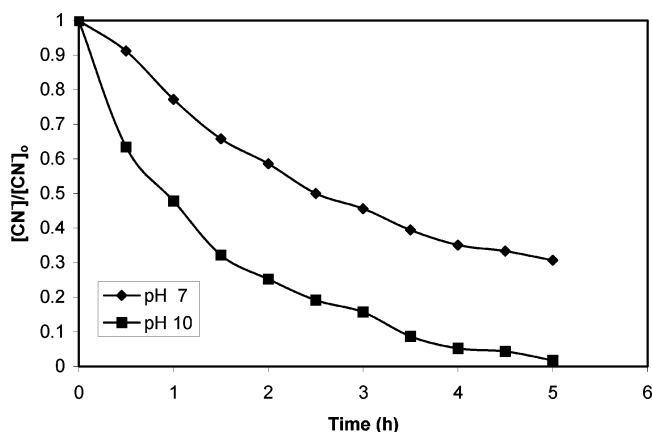
As stated previously, experiments have been conducted in a bipolar stack cell, and the results are presented in Figures 2–5

and Table 1 by varying the operating conditions, such as flow rate, pH, and applied potential. When the effluent with a low concentration of cyanide in an alkaline medium, with the supporting electrolyte NaCl, is circulated in a bipolar stack cell, we assume that indirect oxidation of cyanide occurs in the bulk of the electrolyte, via hypochlorite to a cyanate ion, which is further decomposed to carbonate or carbon dioxide and nitrogen, and a simultaneous reduction of the  $\text{Cd}^{2+}$  ion to cadmium through deposition on the cathodic surfaces of bipolar stack also occurs. At high  $\text{CN}^-$  concentrations, there is the possibility for direct anodic oxidation of cyanide to cyanate and cynogen.<sup>17</sup> The direct electro-oxidation rate of cyanide and cyanate ions is dependent on the catalytic activity of the anode, as well as on the diffusion rate of the ions in the active points of the anode and the applied current density. The indirect electro-oxidation rate of cyanide is dependent on the diffusion rate of the oxidants into the solution, the flow rate of the effluent, the temperature, and the pH. In moderate alkaline solutions, a cycle of chloride  $\rightarrow$  chlorine  $\rightarrow$  hypochlorite  $\rightarrow$  chloride is observed, which produces  $\text{OCl}^-$ .

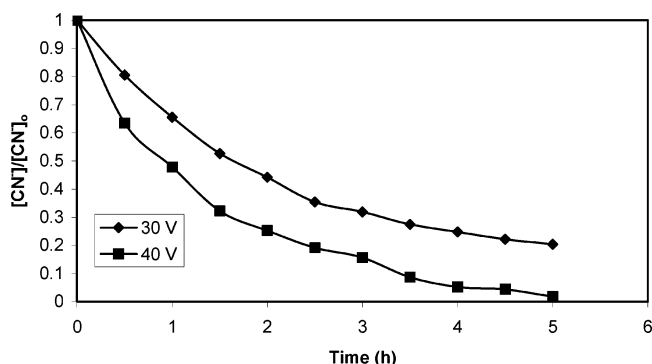
**3.1 Electrochemical Destruction of Cyanide.** In the reservoir, the variation of the extent of unconverted cyanide ion with time—that is, the ratio of  $[\text{CN}^-]/[\text{CN}^-]_0$  versus time—is presented in Figure 2 for five different volumetric flow rates, Figure 4 for two different pH values, and Figure 5 for two different applied potentials.

**3.1.1. Effect of Flow Rate.** Experiments were conducted at five flow rates, keeping other parameters constant. It can be ascertained from Figure 2 that the cyanide concentration decreases as the electrolysis time increases. The rate of decrease of cyanide concentration is larger in the beginning of the process, and it tries to approach a constant value at the end of the process (i.e., after 4 h of electrolysis). Figure 2 also shows that the rate of cyanide degradation increases as the electrolyte circulation rate increases, and the electrolyte concentration of cyanide ion in the bulk of the reactor decreases and reaches a constant value (this does not decrease beyond a flow rate of 180 L/h). The rate of cyanide degradation is dependent on the bulk concentration of cyanide ion. This may be explained as follows: Higher flow rate showed a significant rate of destruction of cyanide, and this may be due to the increased production of oxidants in the process. We have used low concentrations of chloride and cyanide. As the electrolyte circulation rate increases, the transport of the  $\text{Cl}^-$  ion from the bulk to the electrode surfaces increases. This would facilitate  $\text{Cl}_2$  generation, as well as the dissolution of  $\text{Cl}_2$  to form  $\text{OCl}^-$  for reaction with the cyanide ion.

**3.1.2. Effect of pH.** The oxidation of cyanide under different pH conditions gives different degradation rates. The results of the experiments conducted to examine the effect of pH are shown in Figure 3. The removal rate of cyanide is relatively high at pH 10, compared with that at pH 7. The rate of reaction is considerably more in basic solution, because of the ready



**Figure 3.** Effect of pH solution on the variation of the extent of unconverted cyanide with electrolysis time. Conditions:  $[\text{CN}^-]_0 = 240 \text{ mg/L}$ ;  $[\text{Cd}^{2+}] = 5 \text{ mg/L}$ ;  $[\text{NaCl}] = 200 \text{ mg/L}$ ;  $Q = 180 \text{ L/h}$ ; applied potential = 40 V.

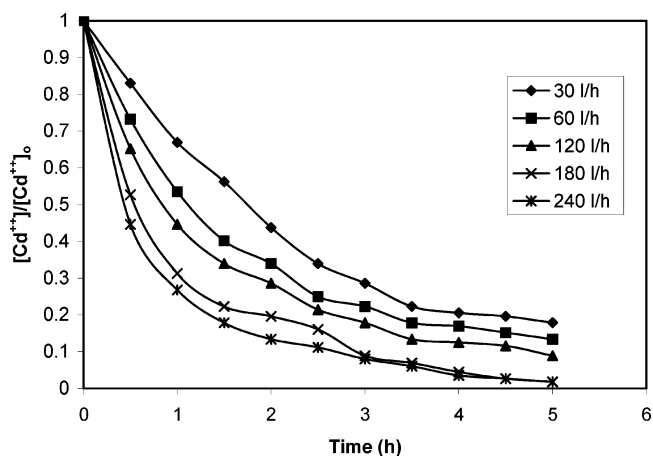


**Figure 4.** Effect of applied potential on the variation of the extent of unconverted cyanide with electrolysis time. Conditions:  $[\text{CN}^-]_0 = 240 \text{ mg/L}$ ;  $[\text{Cd}^{2+}] = 5 \text{ mg/L}$ ;  $[\text{NaCl}] = 200 \text{ mg/L}$ ;  $Q = 180 \text{ L/h}$ ; pH 10.

formation of  $\text{OCl}^-$  ( $\text{p}K_a = 7.44$ ) ion, which implies that the basic pH conditions are more favorable for conducting reactions in which chlorine is evolved.<sup>37</sup> On the other hand, it has been noticed that an increase in pH beyond 10 does not yield any improvement in the rate of cyanide degradation. Thus, the pH of the electrolyte has been maintained at 10 for the remainder of the experiment. Note that if the reaction is conducted at a pH that is too low, there is a possibility of generating cyanogen chloride, which is a very toxic intermediate. For this reason, the chlorination of cyanide is usually conducted at  $\text{pH} > 10$ .

**3.1.3. Effect of Cell Voltage.** Figure 4 shows the removal rate for the anodic oxidation of cyanide, as a function of the applied potential. The current supplied is dependent on the applied potential, which influences the rate of  $\text{Cl}_2$  generation (or the rate of cyanide removal) and the current density is dependent on a heterogeneous rate constant, which can be governed by a simple Tafel-type expression for the applied potential, as might have been expected in any other electrochemical process.

**3.2. Electrochemical Reduction of Cadmium.** In the reservoir, the variation of the extent of unconverted  $\text{Cd}^{2+}$  ion with time—that is, the ratio of  $[\text{Cd}^{2+}]/[\text{Cd}^{2+}]_0$  versus time—is presented in Figure 5 for five different volumetric flow rates, keeping other parameters constant. It can be ascertained from Figure 5 that the cadmium concentration decreases as the electrolysis time increases. Also note from Figure 5 that the rate of cadmium removal increases as the electrolyte circulation rate increases, and the electrolyte concentration of the  $\text{Cd}^{2+}$  ion in the bulk of the reactor decreases and reaches a constant value (where the concentration of  $\text{Cd}^{2+}$  ion at the electrode surface is zero, which is the limiting case); this does not decrease beyond



**Figure 5.** Effect of the flow rates on the variation of the extent of unconverted cadmium ion with electrolysis time. Conditions:  $[\text{CN}^-]_0 = 240 \text{ mg/L}$ ;  $[\text{Cd}^{2+}]_0 = 50 \text{ mg/L}$ ; pH 10;  $[\text{NaCl}] = 200 \text{ mg/L}$ ; applied potential = 40 V.

the flow rate of 180 L/h. The rate of cadmium removal is dependent on the bulk concentration of  $\text{Cd}^{2+}$  ions in the reactor.

**3.3. Power Consumption.** The results, which are presented in Table 1, show that the flow rate of the effluent into the reactor also significantly influences the power consumption. Only a few percent of total energy requirement of the electrochemical step is needed to pump the electrolyte around the electrolyte cycle and a small fraction of the energy is necessary to maintain a sufficiently fast flow through the narrow gaps between the electrodes.<sup>38</sup>

The specific energy consumption for electrolysis,  $P$  (given in units of kWh/kg), is computed using the expression

$$P = \frac{\mathcal{V}_a I t / 10^3}{[(C_0 - C_f) V / 10^6]}$$

where the numerator represents the power input (in kilowatt hours),  $\mathcal{V}_a$  is the applied voltage (given in volts),  $I$  is the current (in amperes) flowing in the circuit, and  $t$  is the duration of electrolysis (in hours) needed to bring the initial concentration of effluent,  $C_0$  (in units of mg/L), to a final concentration  $C_f$  (also given in units of mg/L) in the volume of the reservoir ( $V$ , given in liters). The flow rate of 30 L/h was observed to offer higher power consumption per kilogram of  $\text{CN}^-$  removal (from 240 mg/L to 75 mg/L), whereas at the same flow rate, it was observed that the power consumption per kilogram of simultaneous removal of  $\text{Cd}^{2+}$  ions, from 50 mg/L to 9 mg/L, is minimum. It was noticed that the power consumption per kilogram of cyanide removal decreases as the flow rate increases, up to 180 L/h, and reaches a constant value and no change with respect to increases of flow rate beyond 180 L/h. Furthermore, it is observed that the power consumption per kilogram of cadmium removal increases as the flow rate increases and reaches an optimum value at 120 L/h, and then reaches a constant value and no change with respect to increases in the flow rate beyond 180 L/h. It is interesting to note that, at 180 L/h, the power consumption for the degradation of cyanide from 240 mg/L to 4 mg/L is 393.22 kWh/kg of cyanide (or 94.4 Wh/L of rinse water), and the power consumption for the simultaneous removal of cadmium from 50 mg/L to 1 mg/L is 1893.87 kWh/kg of cadmium (or 94.7 Wh/L of rinse water).

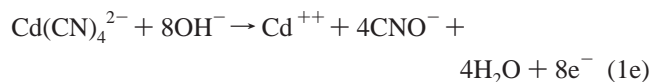
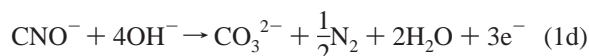
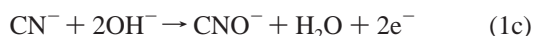
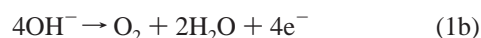
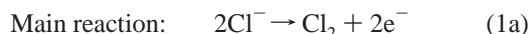
**3.4. Rinsewater Management.** The concentrations of cadmium and cyanide generated due to spray rinsing, drag out of plated articles (in Figure 1b) for each and every washing of



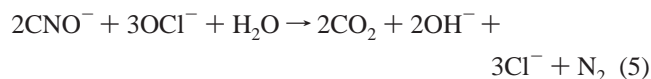
sheets there is build up of concentration in each of the rinse tank. The cadmium and cyanide concentration of the spray tank and drag-out tank (dead tank) is considerably high, compared to the concentration in the rinse tank. That is the reason why the solutions from a drag-out tank are generally used to make up a plating bath, to avoid the loss of proprietary chemicals, such as brighteners that are normally used by plating shops. Moreover, the concentration buildup in the drag-out and rinse tank is dependent on the total area of the plated sheets to be cleaned and the capacity of the wash tank. From the numbers of sheets plated or plated area, and the corresponding concentration rise in each rinse tank (for the given volume of the rinse tank) due to rinsing, a correlation can easily be derived in plant practice. This can help to prepare a schedule of operation of treatment plant in a stack reactor for effective management for recycle of water for rinsing operation. We can continuously remove cadmium and cyanide ions from the rinse water using an electrochemical stack reactor and recycle the water so that water conservation can be achieved. More cadmium can be recovered by anodic stripping periodically.

**3.5. Reaction Mechanism and Reactor Modeling.** In the electrochemical treatment of rinse water that contains cyanide, as well as heavy metals such as cadmium, several possible reactions can occur at the electrodes. In this process, cyanide is oxidized either indirectly via hypochlorite or directly at the anode to a cyanate ion, which is further decomposed to carbonate or carbon dioxide and nitrogen. The reactions are as follows.

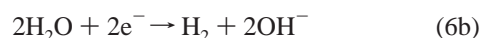
At the anode:



In the bulk of the solution:



At the cathode:



Because cyanide and cyanate ions are not very active electrochemically, the primary reaction that occurs at the anodes is  $\text{Cl}^-$  ion oxidation (eq 1a) with the liberation of  $\text{Cl}_2$ , which is a robust oxidizing agent. Because the wash water is generally basic, in which case the side reaction (eq 1b) occurs, generating

oxygen, which is a relatively weak oxidant and, hence, is not useful in the present context of effluent treatment, and this leads to a reduction in current efficiency. If the reactions happened to occur via eqs 1c and 1d, instead of eqs 4 and 5, there will also be a reduction in current efficiency, because of the formation of cyanate and carbonate ions. The counter reactions (eqs 6a and 6b) that occur at the cathode would be the reduction of the  $\text{Cd}^{2+}$  ion and water only when no other reducible species are present. Equations 1d and 6b occur when complex species are present. In regard to the reactions in the bulk, gaseous  $\text{Cl}_2$  dissolves in the aqueous solutions, because of ionization, as indicated in eq 2. The rate of reaction is considerably greater in basic solution, because of the ready formation of  $\text{OCl}^-$  ion ( $\text{p}K_a = 7.44$ ) in eq 3, implying that the basic or neutral pH conditions are more favorable for conducting reactions that involve chlorine.<sup>37</sup> The indirect electro-oxidation rate of cyanide is dependent on the diffusion rate of the oxidants into the solution, the flow rate of the effluent, the temperature, and the pH. In moderate alkaline solutions, a cycle of chloride  $\rightarrow$  chlorine  $\rightarrow$  hypochlorite  $\rightarrow$  chloride occurs, which produces  $\text{OCl}^-$ . The pseudo-steady-state theory can be applied to each of the intermediate products ( $\text{HOCl}$  and  $\text{OCl}^-$ ) taking part in the bulk solution. Then, we denote  $r_i$  as the rate of reaction  $i$  for the sequence

$$-r_{\text{Cl}_2} = k_2[\text{Cl}_2] \quad (7)$$

$$r_{\text{HOCl}} = k_2[\text{Cl}_2] - k_3[\text{HOCl}] + k'_3[\text{H}^+][\text{OCl}^-] = 0 \quad (8)$$

$$r_{\text{OCl}^-} = k_3[\text{HOCl}] - k'_3[\text{H}^+][\text{OCl}^-] - k_4[\text{CN}^-][\text{OCl}^-] - k_5[\text{CNO}^-][\text{OCl}^-] = 0 \quad (9)$$

$$r_{\text{CNO}^-} = k_4[\text{CN}^-][\text{OCl}^-] - k_5[\text{CNO}^-][\text{OCl}^-] = 0 \quad (10)$$

$$-r_{\text{CN}^-} = k_4[\text{CN}^-][\text{OCl}^-] \quad (11)$$

Using eqs 8–10, we then can easily deduce the following expression:

$$\frac{-r_{\text{Cl}_2}}{2} = -r_{\text{CN}^-} = k'_4[\text{CN}^-][\text{OCl}^-] \quad (12)$$

From the material balance of the main equation (eq 1), we can relate  $-r_{\text{Cl}^-}/2 = r_{\text{Cl}_2}$ , and, finally, we can rewrite it as

$$\frac{-r_{\text{Cl}_2}}{2} = \frac{r_{\text{Cl}^-}}{4} = \frac{k_2[\text{Cl}_2]}{2} = -r_{\text{CN}^-} = k_4[\text{CN}^-][\text{OCl}^-] \quad (13)$$

where the rate of reaction  $r_i$  and the rate constants  $k_i$  (for  $i = 2, 3, 4$ , and  $5$ ) are defined, with respect to the bulk and the rate expression for the main electrode reaction, per eq 1, can be rewritten as

$$-r'_{\text{Cl}_2} = \frac{r'_{\text{Cl}^-}}{2} = k_1[\text{Cl}^-] \quad (14)$$

where  $k_1$  is the heterogeneous electrochemical rate constant. Hence, in the following section, an attempt has been made to establish a relationship between the reacting species in the bulk and that at the electrode surfaces. The basic relationship applicable to all electrochemical reactions is Faraday's law, which relates the amount of substance reacted at the surface to the charge ( $I_A t$ ) passed is  $M_A I_A t / nF$  (assuming 100% current efficiency) and the characteristic measurable parameter is current density,  $i_A$ , which is defined as  $i_A = I_A / A_e$ . Thus, the electro-

chemical reaction rate (for the disappearance of reactant A) can be expressed as

$$-\left(\frac{V_R}{A_e}\right)\frac{d[A]}{dt} = \frac{i_A}{nF} \quad (15)$$

where  $I_A$  is the current passed in time  $t$ ,  $M_A$  the molecular weight,  $n$  the number of electrons transferred per mole of reaction,  $A_e$  the electrode area,  $V_R$  the reactor volume, and  $F$  the Faraday constant ( $F = 96\,500$  C or As/mol). Note that

$$-r_A = -\frac{d[A]}{dt} = \frac{i_A a}{nF}$$

where  $a$  is the specific electrode area (defined as  $a = A_e/V_R$ ). Assuming that the main electrode reaction is governed by a simple Tafel-type expression, then

$$-\left(\frac{V_R}{A_e}\right)\frac{d[A]}{dt} = \frac{i_A}{nF} = k'[A] \exp(bE) \quad (16)$$

$$-\frac{r'_{Cl^-}}{2} = r'_{Cl_2} = k_1[Cl^-] = k'_1 a [Cl^-]_s \exp(bE) \quad (17)$$

The reaction may be assumed to be under mixed control, because the data show that both the voltage and the recirculation rate affect the reaction rate. The reactant  $Cl^-$  ion is transported from the bulk to the electrode surface, where it undergoes electrochemical oxidation to  $Cl_2$  and it may be transported back to the bulk via a diffusion reaction in the bulk. Then,

$$\frac{i_A}{zF} = k_L([Cl^-] - [Cl^-]_s) \quad (18)$$

The elimination of  $[Cl^-]_s$ , using eqs 16 and 17, results in

$$\frac{i_A}{zF} = k[Cl^-] \quad (19)$$

where

$$\frac{1}{k} = \frac{1}{k_L} + \frac{1}{k'_1 \exp(bE)} \quad (20)$$

From a material balance of species  $Cl^-$ , by taking note of eqs 12 and 13, we can write

$$\frac{i_A}{zF} = k'[Cl_2] \quad (21)$$

$$\frac{i_A}{zF} = k''[CN^-][OCl^-] \quad (22)$$

During electrolysis, because a constant potential or current is applied, the rate of generation of  $[OCl^-]$  will remain constant, under a given set of experimental conditions; however, it varies as the applied potential or current is altered. Then,

$$\frac{i_A}{zF} = k_{obs}[CN^-] \quad (23)$$

Because of the fact that  $Cd^{2+}$  ions are electrochemically active, the primary reaction that occurs at the cathode is electrochemical reduction of the  $Cd^{2+}$  ion (eq 6). With the wash water being generally basic or neutral, the parallel cathodic reaction (eqs 6a) occurs and generates hydrogen. This may lead to a decrease in cathodic current efficiency.

Because the concentration of cadmium present in the wash water is low, the electrode potential and the electrolysis conditions refer to a lean solution of metal ions and are fixed so that the removal of cadmium is completely mass-transfer-controlled. The disc cathode is then operated at its maximum duty, corresponding to the limiting current  $I_L$ , which may be expressed in terms of mass-transfer coefficient ( $k_L$ ), the electrode area ( $A$ ), and the bulk  $Cd^{2+}$  ion concentration ( $[Cd^{2+}]$ ), i.e.,

$$\frac{i_A}{zF} = \frac{I_L}{zFA} = k_L[Cd^{2+}] \quad (24)$$

It is further assumed that the entire cathode surface is active, and the reactor performance is characterized by the factor  $k_L a$ , where  $a$  is the total cathode area per unit volume of the reactor, which may be determined by direct measurement of the limiting current  $I_L$  at a known concentration, followed by application of a rearranged form of the previously mentioned eq 24. This relation may be written as

$$\frac{I_L}{zFV_R[Cd^{2+}]} = k_L a \quad (25)$$

The mode of operation of the bipolar disc stack reactor, as depicted in Figure 1, involves continuous recirculation of the rinse water. There is a gradual depletion of the concentration of the cyanide and  $Cd^{2+}$  ions in the reservoir. To design the plant for treatment processes, the development of the model is essential, which permits prediction of the variation of concentration of the cyanide and  $Cd^{2+}$  ions, with time, in the reservoir. The basic assumptions involved in the ensuing derivation may be outlined as follows.

A back-mix flow exists in the present reactor system. It was determined based on a tracer experiment known as residence time distribution (RTD) method. An approximate model that represents the given bipolar disc stack reactor in which the reactions occur is described by a continuously stirred tank reactor (CSTR). The dynamic material balances to each of the component or species at reactor can be written as

$$\begin{aligned} \text{rate of change mass of species in the reactor} = \\ (\text{rate of mass input}) - (\text{rate of mass output}) \mp \sum \\ (\text{rate of mass of species disappeared or} \\ \text{generated during chemical reactions}) \end{aligned}$$

The reservoir is assumed to be a perfectly back-mixed system. The concentration variation of cyanide/ $Cd^{2+}$  ions in the reactor can be written as

$$V_R \left( \frac{dC'}{dt} \right) = QC - QC' - kA_e C' \quad (26)$$

The left-hand side (LHS) of the equation represents the rate of change of mass of cyanide/ $Cd^{2+}$  ions in the free volume of reactor,  $V_R$  is the free volume of the reactor, and  $C'$  is the concentration of cyanide/ $Cd^{2+}$  ions leaving the reactor. The first two terms of the right-hand side (RHS) of the equation represent the mass rate of cyanide/ $Cd^{2+}$  ions entering and leaving the reactor, whereas  $Q$  is the volumetric flow rate and  $C$  is the concentration of cyanide/ $Cd^{2+}$  ions. The last term in the RHS of the equation represents the rate of disappearance of mass in the solution due to reaction. The mass balance for the effluent reservoir is

$$V\left(\frac{dC}{dt}\right) = QC' - QC \quad (27)$$

Furthermore, it can also be assumed that the reactor is under steady-state conditions, and eq 26 can be rewritten as

$$\tau_R = \frac{V_R}{Q} = \frac{C - C'}{kaC'} \quad (28)$$

where  $a$  is the specific electrode area ( $a = A_e/V_R$ ), and eq 28 can be rewritten as

$$\frac{C'}{C} = \frac{1}{1 + ka\tau_R} = \frac{1}{1 + (ka_e/Q)} \quad (29)$$

The mass balance eq 27 can be solved. After substitution of an expression for  $C'$  from eq 29, knowing the initial concentration is  $C = C_o$  at  $t = 0$ , the resultant equation can be written as

$$\frac{C}{C_o} = \exp\left\{-\frac{t}{\tau}\left[\frac{ka_e/Q}{1 + (ka_e/Q)}\right]\right\} \quad (30)$$

where  $C_o$  is the initial concentration of cyanide/ $\text{Cd}^{2+}$  ions in the reservoir.

Note that the extent of conversion is defined as  $X = (C_o - C)/C_o$ . The unconverted species ( $1 - X$ ), which is equal to  $C/C_o$ , decreases exponentially with time.

According to eq 30, the slope of the plot of  $\ln(C/C_o)$  vs  $t$ , or  $\ln(1 - X)$  vs  $t$ , gives the value  $(ka_e/Q)/[\tau(1 + ka_e/Q)]$ , from which the value of  $k$ , which is the pseudo-mass-transfer coefficient, may be computed. The results obtained are presented in Table 1, with respect to cyanide oxidation as well as cadmium reduction. The increase in flow rate of effluent into the reactor significantly increased the value of the mass-transfer coefficients, which resulted in a higher extent of fractional conversions.

#### 4. Conclusions

Bipolar disc stack reactors have attracted great interest, because of their simple geometry. The radially divergent flow in gaps will highly enhance the rate of electrochemical reaction for low-conducting fluids. A planar radially symmetric flow is enforced at the inner edge of the disc and directed outward through gaps. As the flow proceeds in the radial direction, the channel is widened, in proportion to the increasing radius. Therefore, we have a laminar decelerating divergent flow. Using the continuity equation (in cylindrical coordinates:  $v_r/r + \partial v_r/\partial r + \partial v_z/\partial z = 0$ ), we can compute the average velocity<sup>38</sup> in the gap (of distance  $s$ ; see Figure 1) from the following:

$$u = \frac{Q}{nA_m}$$

where

$$A_m = \frac{A_o - A_i}{\ln(A_o/A_i)}$$

$$A_o = 2\pi R s$$

and

$$A_i = 2\pi r s$$

Furthermore, the average mass-transfer coefficient can be obtained using the relation  $k = au^b$ ; Table 1 shows that, for

cyanide oxidation,  $b = 0.44$  and, for the electrochemical reduction of cadmium,  $b = 0.32$ . In the case of the electrochemical oxidation of cyanide, this may be theoretically explained by applying Ruckenstein's renewal model,<sup>39</sup> where  $k$  is dependent on  $u^{0.5}$ . This model assumes zones of good mixing from which the boundary layer grows anew. In our system, the generation of hydrogen, oxygen, and chlorine is responsible for the creation of good mixing zones in the gaps of a bipolar disc stack. With regard to the value of  $b = 0.32$  for the electrochemical reduction of the  $\text{Cd}^{2+}$  ion, this observation indicates that the mass-transfer rates for the flow channel may be expressed theoretically using a Leveque-type equation,<sup>39</sup> in which  $k_L$  is dependent on  $u^{0.33}$ . Only a few percent of the total energy requirement of the electrochemical step is needed to pump the electrolyte around the electrolyte cycle. Most of it is consumed, to overcome the pressure drop in filters, flow meters, and control valves, and only a small fraction of the energy is necessary to maintain a sufficiently fast flow through the narrow gaps between the electrodes.<sup>38</sup> A list of symbols is presented in the Nomenclature section at the end of this paper for immediate reference.

Experiments have been conducted in a bipolar electrochemical cell covering different ranges of operating conditions. It has been concluded from the present investigation that >99% cyanide destruction, with 98% cadmium removal, has been achieved under optimum condition using this electrochemical cell. The results indicate that the cyanide present in the effluent can be destroyed with the simultaneous removal of cadmium. Thus, it can be concluded that the electro-oxidation of cyanide, with a simultaneous metal-ion deposition technique, can be effectively applied to remove cyanide present in the effluent with other heavy metals.

#### Nomenclature

$a$  = specific electrode area;  $a = A_e/V_R$   
 $A_e$  = electrode area  
 $b$  = Tafel parameter  
 $C_o$  = initial concentration  
 $C'$  = reservoir entry concentration or reactor exit concentration  
 $C$  = reservoir exit concentration or reactor entry concentration  
 $E$  = electrode potential  
 $F$  = Faraday constant (96 500 C/mol or As/mol)  
 $I$  = current  
 $I_L$  = limiting current  
 $i, i_A$  = current density  
 $k, k_L$  = transfer coefficient  
 $k_i$  = reaction rate constant of bulk  
 $k'_i$  = surface reaction rate constant  
 $n, z$  = number of electrons exchanged  
 $P$  = specific energy consumption  
 $Q$  = volumetric flow rate  
 $r_i$  = rate of the reaction of species  $i$  in bulk  
 $r'_i$  = rate of the reaction of species  $i$  in the electrode surface  
 $R$  = coefficient of correlation  
 $r$  = inner radius of disc  
 $R$  = outer radius of disc  
 $s$  = capillary gap  
 $t$  = time  
 $u$  = mean electrolyte velocity in gap  
 $\mathcal{V}_a$  = applied voltage  
 $V$  = reservoir volume  
 $V_R$  = free volume of reactor  
 $X$  = extent of conversion

$\tau_R$  = reactor residence time;  $\tau_R = V_R/Q$   
 $\tau$  = reservoir residence time;  $\tau = V/Q$

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