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Enhanced precipitation of cyanide from electroplating wastewater via self-assembly of bimetal cyanide complex

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ABSTRACT

A novel and cost-effective technology has been developed to enhance cyanide (CN) removal from electroplating wastewater. In this process, CN and Zn wastewater was proportionally mixed with Ni wastewater at a controlled pH for precipitation. As a result, 99% of CN and 85% of Zn were removed from the simulated test. Characterizations of XRD and FTIR displayed that CN and Zn removals were attributed to the formation of ZnNi bimetal cyanide complex. When this method was applied to the treatment of CN and Zn electroplating wastewater, 75% of CN and 100% of Zn were synchronously removed by forming a mixture of ZnNi bimetal cyanide complex and NiZnOH. Furthermore, mechanism analyses showed that CN first transformed into $Ni(CN)_4^{2-}$, then precipitated into bimetal cyanide complex. This work revealed that the presented strategy is an effective approach for the purification of both cyanide and heavy metal from electroplating wastewater.

1. Introduction

Cyanide (CN) is widely used in electroplating industry, because it can assure the high quality of electroplated product. Thus, CN usually co-exists with heavy metal in the electroplating wastewater. Since CN can easily coordinate with various metals, such as Zn, Fe and Ni, it generally exists in the chemical forms of both free and coordinated states in the wastewater. Without proper treatment, CN is quite lethal to animals and humans. The co-existence of cyanide and heavy metal in the wastewater causes high toxicity to both environment and human being [1]. Hence, this kind of wastewater must be properly treated before it could be safely disposed, or even discharged.

Generally speaking, chemical precipitation is one of the most widely used technology in the treatment of heavy metal wastewater. At the same time, chemical precipitation is also one of the most cost-effective technologies. However, cyanide and heavy metal co-existing wastewater is rather difficult to deal with, because the strong CN-metal bond must be broke first before chemical precipitation could be effectively applied. Until recently, several effective methods have been proposed for disposal of CN containing wastewater, such as alkaline chlorination, chemical oxidation, adsorption and ion-exchange [2–5]. However, these methods still have disadvantages. For example, alkaline chlorination would generate toxic by-product CNCl [6]. Therefore, it is urgently necessary to develop cost-effective and reliable method for handling cyanide and heavy metal co-existing wastewater.

A novel method has was applied to the treatment of CN containing wastewater by co-precipitation of layered double hydroxide (LDH) in our previous study, and 50–60% of total cyanide was removed [7]. In order to increase CN removal, Ni was then utilized to convert free and coordinated CN^- into $Ni(CN)_4^{2-}$, since $Ni(CN)_4^{2-}$ has stronger affinity for LDH interlayer than free CN^-. Thus, CN was removed by forming $Ni(CN)_4^{2-}$ intercalated LDH. Fortunately, removal of total CN was above 90%, when the initial cyanide was 5–25 mg/L. However, when the initial CN increased to 100 mg/L, only 60% of CN was removed. Besides, additional Al reagent was used to form LDH precipitation, which increased the operation cost.

Recently, bimetal cyanide complex (BMCC, Prussian blue analogue) and double metal cyanide bridging complex are reported to be promising catalysts [8,9]. These materials could be easily synthesized by co-precipitation. Since CN either co-exists with heavy metal (such as zinc) as the complex form or exist as free cyanide in the electroplating wastewater, we here suggested a novel

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method for removing CN and heavy metal by forming bimetal cyanide complex. With this method, cyanide and heavy metal could be treated at the same time, requiring neither breaking Zn–CN bond by oxidization nor adding extra metal reagents.

Therefore, in this research, we investigated the possibility of enhancing CN removal from cyanide and heavy metal containing wastewater by self-assembly of bimetal cyanide complex. Objectives of this research were to (1) detect the removal of cyanide and heavy metal from simulated CN and Zn wastewater by precipitating BMCC; (2) compare the removals of cyanide and heavy metal by forming BMCC and LDH from electroplating wastewater; and (3) understand the technology for the formation of BMCC from cyanide and heavy metal co-existing wastewater.

2. Materials and methods

2.1. Electroplating wastewaters

Two kinds of electroplating wastewaters were supplied by Shanghai Xinsheng Electroplating Co., Ltd. Table 1 lists the main components and their concentrations in these two wastewaters. In general, one electroplating wastewater mainly contained 55.2 mg/L of Zn and 94.1 mg/L of cyanide, the other one mainly contained 271.0 mg/L of Ni, and they were denoted as ZC-EW and Ni-EW respectively. In particular, free, complex and total concentrations of cyanide were simplified as CN_f, CN_c and CN_t.

2.2. Removal of CN and Zn from simulated wastewater

A simulated solution was first prepared by dissolving KCN and $Zn(CN)_2$ at pH = 11.0. It contained 215.6 mg/L (8.2 mmol/L) of CN_t and 137.8 mg/L (2.2 mmol/L) of Zn. Then, 5 ml of liquid with 2582.4 mg/L (44 mmol/L) of Ni was added into 100 ml of simulated solution, i.e. the molar ratio of Ni:Zn:CN was 1:1:4. After this process, the mixed solution was stirred continuously under N_2 atmosphere for 30 min, aged for 16 h at 60 °C to form precipitation. Other simulated tests were applied in similar method, except that Ni:Zn molar ratio was adjusted from 2:1 to 6:1, and initial pH was controlled from 11.5 to 13. The samples precipitating at pH = 11.0 were simplified as Ni*x*Zn-S (*x* = 2–4). Furthermore, in order to compare the products obtained from the above processes, NiZn-hydroxide with Ni:Zn molar ratio = 1:1 was synthesized at pH = 11.0 by co-precipitation.

2.3. Removal of CN and Zn from real electroplating wastewater

The method used in simulated tests was utilized to remove CN and Zn from real electroplating wastewater. There was 94.1 mg/L of CN_t, 47.9 mg/L of CN_f and 55.2 mg/L of Zn in ZC-EW. In order to adjust Ni:Zn = 2:1–6:1, 100 ml of ZC-EW was mixed with 5 ml of diluted Ni-EW at pH = 11. The mixed solution was stirred continuously under N_2 atmosphere for 30 min, aged for 16 h at 60 °C. These samples were simplified as Ni*x*Zn-R (*x* = 2–6).

For comparison, ZC-EW was also treated by LDH-precipitation method. Two solutions were first prepared. Solution A contained 20 mmol/L of $Zn(NO_3)_2/Mg(NO_3)_2$ and 10 mmol/L of $Al(NO_3)_3$. Solution B was mixed by ZC-EW and Ni-EW. In brief, the initial CN_t of ZC-EW was diluted from 94.1 to 23.4, 9.4 and 4.7 mg/L. Then, in order to transform CN^- and $Zn(CN)_4^{2-}$ into $Ni(CN)_4^{2-}$, diluted Ni-EW (Ni:Zn molar ratio = 1:1) was added into these ZC-EW samples. The pH was controlled at 11.0. Then, 200 ml of solution B was mixed with 10 ml of solution A under vigorous stirring for 10 min to form LDH.

Table 1
Main components and their concentrations (mg/L) in electroplating wastewater.

	CN_t	CN_f	Mg	Ca	Ni	Zn	Al	pH
ZC-EW	94.1	47.9	3.6	5.0	3.5	55.2	4.1	12.4
Ni-EW	N.D.[a]	N.D.[a]	2.4	30.1	271.0	2.0	0.5	4.7

[a] N.D. stands for “not detected”.

2.4. Determination of metal and cyanide concentration

All the obtained mixtures were separated by centrifugation. Centrifuged supernatants were stored in high-density polyethylene (HDPE) vessels for the determinations, including final pH, residual metal concentration, CN_f and CN_t. The resultant precipitations were dried at 80 °C in a vacuum oven and stored in desiccator for further characterizations.

Metal concentrations in wastewater before and after treatment were detected by inductively coupled plasma atoms emission spectrometer (ICP-AES, Leeman Co., USA). CN_f was determined by spectrophotometer method [10]. Similarly, CN_t was obtained by spectrophotometer after cyanide distillation in a UNICO UV-spectrophotometer (4802UV/VIS). The difference between CN_t and CN_f was CN_c.

2.5. Characterizations

Precipitations were characterized by XRD and FTIR. XRD patterns were collected on a Rigaku D/max RBX X-ray diffractometer with Cu K radiation ($\lambda = 0.154$ nm) at a scanning rate of 6°/min from 5° to 80°. FTIR (Fourier Transform Infrared Spectra) were recorded on a Nicolet 380 spectrometer (Thermo Scientific Co.) in the range from 400 to 4000 cm^{-1}. Each spectrum was obtained after overlapping 128 scans at a resolution of 4 cm^{-1} by measuring the IR absorbance of KBr disc containing 1–2 wt% sample.

FTIR of solution was gotten from a thin film of sample that was held by two CaF_2 discs in a liquid cell. Each spectrum was overlapped by 128 scans at a resolution of 4 cm^{-1} by measuring the IR absorbance of the liquid film. Residual solution of Ni*x*Zn-S (*x* = 2–4) were characterized by aquatic FTIR. Furthermore, several solutions were also prepared to investigate the transformation of free cyanide into coordinated cyanide at pH = 11.0, including 4 mmol/L KCN, 2 mmol/L KCN+1 mmol/L $Zn(CN)_2$, 4 mmol/L KCN+1 mmol/L Ni^{2+} and 2 mmol/L KCN+1 mmol/L $Zn(CN)_2$+1 mmol/L Ni^{2+}. Besides, in order to speculate the formations of $Zn(CN)_4^{2-}$ and $Ni(CN)_4^{2-}$, equilibrium components of the solutions were detected, including 2 mmol/L KCN + 1 mmol/L $Zn(CN)_2$ and 4 mmol/L KCN+1 mmol/L Ni^{2+}. In these two solutions, Zn:CN and Ni:CN molar ratios were regulated from 0.05 to 0.25.

3. Results and discussion

3.1. Removal of CN and Zn in simulated test

Fig. 1A shows CN and Zn removal after adding Ni (Ni:Zn molar ratio = 1:1), when initial pH was adjusted from 11.5 to 13.0. In general, CN_f removal was around 80% within the tested pH ranges. However, only 10–25% of CN_t was removed. For example, initial CN_f and CN_t was 4.6 and 8.2 mmol/L at pH = 11.5, which indicated that approximately 50% of CN_t existed as CN_f. After adding Ni, CN_f and CN_t decreased by 3.86 and 2.02 mmol/L, respectively. The difference between removals of CN_f and CN_t revealed that most CN_f transformed into CN_c, and CN_c was left in the solution in the form of metal cyanide complex, such as $Ni(CN)_4^{2-}$ and $Zn(CN)_4^{2-}$. On the other hand, Zn removal decreased from 81.5% to 26.7%, when the pH increased from 11.5 to 13.0, since partial Zn would still exist as zinc hydroxyl in the solution at pH > 10. This also explained why Zn is very difficult to deal with co-precipitation during the