Toxicity identification of effluent from a semiconductor lead frame manufacturing factory

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A B S T R A C T

The acute toxicity of lead frame effluent to Daphnia magna was found to be 22.62 TU, which far exceeded the toxicity discharge limit in Korea (<1 TU). TIE phases I and II result suggest that the mixture of Ag, Cu and CN were likely responsible for the observed toxicity, and this was confirmed by mass balance approach (TIE phase III). In addition, the Visual MINTEQ simulation suggested the presence of $[Ag(CN)_2]^-$ and $[Cu(CN)_3]^{2-}$ complexes in the effluent. Therefore, TIE procedures with chemical speciation modeling were effective for identifying the cause of acute toxicity in industrial effluents.

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1. Introduction

Lead frames are generally constructed from metal alloy strips by either a stamping or etching process, followed by cleaning, silver-plating, taping and downsetting steps. As a result, the wastewater from the lead frame manufacturing process contains appreciable amounts of toxic metals (Ag, Cu, Ni, etc.) and cyanide ions (CN^-) [1]. Discharging this kind of industrial effluent can have adverse effects on the waterbodies, however physicochemical analysis alone is limited to assessing the ecological effects of the effluent [2]. Accordingly, the Korea Ministry of Environment has implemented new criteria using Daphnia magna acute toxicity tests to regulate and manage wastewater effluents from industries since 2011 [3].

In addition, toxicity identification evaluation (TIE) methods are useful to characterize and identify toxicity-causing substances, since not all of the compounds in wastewater effluents are responsible for the observed toxicity [4]. The TIE was developed by USEPA [5–7] and has been widely used to identify and reduce the major toxicants in industrial effluents [8,9]. For instance, Yi et al. [10] successfully identified the causes of toxicity in effluents from a metal plating factory and a rubber products factory as Zn^{2+}, Cl^- and $SO_4{}^{2-}$.

However, to the best of our knowledge, there have been no studies which attempted to identify the cause of the toxicity in the effluent from a lead frame manufacturing factory. Moreover, the mixture toxicity of the various toxicants (heavy metals, cyanide ions, etc.) in this effluent needs to be clearly characterized. Thus, the objectives of this study were (1) to identify the major toxic substances in lead frame effluents using TIE procedures and (2) to reveal the underlying chemistry of the toxicity in the lead frame effluent.

2. Experimental

2.1. Sample collection and chemical analyses

Copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$, 99%) and potassium cyanide (KCN, 98%) were purchased from Junsei Chemical Co., Ltd. (Japan), and silver nitrate ($AgNO_3$, 99.9%) was obtained from Kojima Chemicals Co., Ltd. (Japan). All of these chemicals were used without further purification.

Grab samples of the effluent from a lead frame manufacturing factory located in Busan, Korea were collected in December 2010. This factory treats about 4300 m^3/d of wastewater using oxidation, neutralization, coagulation/flocculation and sedimentation processes. The samples were transported in a polyethylene container and immediately stored at 4 °C. Initial toxicity tests and water quality analyses were conducted upon the arrival of the sample.

The dissolved organic carbon (DOC) was analyzed after filtering through a 0.45 μm syringe filter, using a Shimadzu TOC analyzer

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(model 5000A, Tokyo, Japan). In addition, the metals were analyzed using a Varian inductively coupled plasma-optical emission spectrophotometer (ICP-OES, Varian Vista PRO, CA, USA). For the metal analysis, all of the vessels and experimental apparatuses were rigorously acid-washed before use. Calibration curves were established daily using freshly prepared standard solutions and the r^2 values of all of the curves were greater than 0.995. The total cyanide (free cyanide ions plus cyanocomplexes) concentration was determined through a standard colorimetric method using a pyridine–pyrazolone mixture to form a highly colored complex with maximum absorbance at 630 nm [11].

2.2. Toxicity testing

Acute toxicity tests were conducted according to the Organization for Economic Co-operation and Development (OECD) standard procedure [12]. Daphnids were grown in the laboratory with 16 h light and 8 h dark periods at 20 ± 2 °C in Elendt M4 medium. Each toxicity test consisted of five dilutions (100%, 50%, 25%, 12.5% and 6.25%) and one control with four replicates per treatment, and each test vessel contained 10 mL of the test solution and five neonates ($\leq$24 h old). Dilution and control water (pH = 7.8 ± 0.1 and hardness = 250 ± 25 mg L^{-1} as CaCO$_3$) was prepared as described by the International Organization for Standardization [13].

Toxicity tests were conducted at 20 ± 2 °C with a 16 h light and 8 h dark photoperiod for 24 h. Immobilization data were employed to calculate the EC$_{50}$ (50% effective concentration) values using Probit analysis, the Trimmed Spearman–Karber Method or a graphical method [14]. The EC$_{50}$ values were transformed into toxic units (TU = 100/EC$_{50}$) for the purpose of comparison.

2.3. Toxicity identification

A toxicity identification evaluation was conducted according to the TIE procedures developed by the USEPA with some modifications. In the TIE phase I test [5], a baseline test, pH adjustment, pH adjustment/aeration, pH adjustment/filtration, pH adjustment/solid phase extraction (SPE), graduated pH, ethylenediaminetetraacetic acid (EDTA) addition and sodium thiosulfate (STS) addition were included to characterize the classes of toxicants. The pH adjustment/aeration manipulation was performed over 60 min at a flow rate of 500 mL min^{-1}, and the pH adjustment/SPE manipulation was conducted at a flow rate of 10 mL min^{-1} using a C$_{18}$ column (Discovery, USA). The EDTA and STS addition manipulations were carried out at different concentrations ranging from 15 to 212 mg L^{-1} of EDTA and 9.5 to 1250 mg L^{-1} of STS.

In addition, ion exchange manipulations were conducted to further characterize the toxicants according to the method described by Jo et al. [8]. Cation and anion exchange columns were prepared with 60 mL syringes filled with either cation (Amberlite IR-120H, Aldrich, USA) or anion (Amberlite IR-410, Aldrich, USA) exchange resins. For the mixed-bed ion exchange manipulation, samples were passed through both anion and cation exchange columns consecutively. Except for the graduated pH tests, the pH of the samples following each manipulation was readjusted to the initial pH with NaOH and HCl before the toxicity test.

In the TIE phase II test [6], those metals suspected as key toxic materials were measured using a Varian ICP-OES. For the metal analyses, aliquots were saved and preserved with concentrated nitric acid. Based on the results of the identification, the suspected toxicants were confirmed by the mass balance approach of the TIE phase III test [7]. For this, toxicity tests were conducted after the addition of the suspected toxicants in the same concentrations as those found in the effluent sample. In addition, a visual MINTEQ program (version 3.0) was used to calculate the chemical species of

Table 1
Chemical characteristics and toxicity of effluents from a lead frame manufacturing factory.

Parameters		Heavy metals		
		Total	Dissolved	EC$_{50}$ (24 h)
TU (24 h)	22.62	–[a]	–	–
pH	5.8	–	–	–
DO (mg L^{-1})	8.64	–	–	–
DOC (mg L^{-1})	25.94	–	–	–
Hardness (mg L^{-1} as CaCO$_3$)	124.1	–	–	–
CN (mg L^{-1})	0.036	–	–	0.609[b]
Ag (mg L^{-1})	–	0.045	0.024	0.023[c]
Cu (mg L^{-1})	–	0.054	0.021	0.022[d]

[a] Not applicable.
[b] Lilius et al. [21].
[c] Khangarot and Ray [22].
[d] Yi et al. [10].

the suspected toxicants in order to interpret their mixture toxicity, with stability constants being accompany the program.

3. Results and discussion

3.1. Acute toxicity of effluent

Chemical and toxicological properties of effluents from a lead frame manufacturing factory are given in Table 1. The effluent showed very high toxicity (22.62 TU) to *D. magna* (Table 1), although the pH, DO and hardness concentrations were at an acceptable level. Moreover, the effluent toxicity far exceeded the new toxicity-based permission criteria, which states that the toxic unit for Class I industrial effluents (>2000 m^3/d) should be less than 1 [3]. Among the toxic metal ions determined, the Ag and Cu concentrations are near to their EC$_{50}$ concentrations (0.023 and 0.022, respectively) and appeared to be related to the initial toxicity.

Ag, which is well known for its toxicity toward *D. magna*, mainly originated from the photographic and imaging industry and electronics manufacturing [15]. In particular, Ag nanoparticles are now widely used in many consumer products including catalysts and disinfectants, and Jo et al. [16] demonstrated that the silver ions dissolved from the Ag nanoparticles are largely responsible for their observed acute toxicity. Cu is a toxic metal widely found in industrial effluents from metal plating factories [10] and electronics [17] and liquid crystal display (LCD) manufacturers [18]. Particularly, we found that the Cu in the LCD wastewater was not effectively reduced to below the toxic levels by the coagulation/flocculation process [18].

3.2. Toxicity identification of effluent

The toxicity characterization (TIE phase I) results of the effluent of the lead frame manufacturing factory are illustrated in Fig. 1. There was no drastic change in toxicity after pH adjustment, pH adjustment/aeration and graduated pH manipulations, indicating that toxicants were unlikely volatile or pH-dependent compounds including ammonia [4]. However, the acute toxicity was completely removed by anion exchange (Anion), mixed-bed ion exchange (Mixed-bed) and sodium thiosulfate (STS) addition. Additionally, several manipulations, such as adjustment of the pH and filtration and cation exchange substantially reduced the effluent toxicity. These results suggest that the toxicants were likely cationic metals, anionic ions and oxidative compounds.

As indicated in Table 1, Ag and Cu are suspect toxicants among cationic metals presented in the effluent, due to their dissolved concentrations near to EC$_{50}$ values. Thus, the Ag and Cu