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TOXICITY IDENTIFICATION AND CONFIRMATION OF METAL PLATTING WASTEWATER

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Abstract : Toxicity of metal plating wastewater was evaluated by using acute toxicity tests on *Daphnia magna*. To identify toxicants of metal plating wastewater, several manipulations such as solid phase extraction (SPE), ion exchange and graduated pH adjustment were used. The SPE test had no significant effect on baseline toxicity, suggesting absence of toxic non-polar organics in metal plating wastewater. However, anion exchange largely decreased the baseline toxicity by 88%, indicating the causative toxicants were inorganic anions. Considering high concentration of chromium in metal plating wastewater, it is thought the anion is Cr(VI) species. Graduated pH test showing independence of the toxicity on pH change strongly supports this assumption. However, as revealed by toxicity confirmation experiment, the initial toxicity of metal plating wastewater (24-h TU = 435) was not explained only by Cr(VI) (24-h TU = 725 at 280 mg L^{-1}). Addition of nickel (29.5 mg L^{-1}) and copper (26.5 mg L^{-1}) largely decreased the chromium toxicity up to 417 TU, indicating antagonistic interaction between heavy metals. This heavy metal interaction was successfully predicted by an equation of 24-h TU = 3.67 × ln([Cu] + [Ni]) + 79.44 at a fixed concentration of chromium.

Key Words : Bioassay, *Daphnia magna*, Heavy metals, Metal plating wastewater, Toxicity identification

INTRODUCTION

Quality control of wastewater in Korea is based on global parameters such as biochemical oxygen demand (BOD), chemical oxygen demand (COD) and suspended solid (SS), and the detection of specific pollutants such as phenol, PCBs, and heavy metals. However wastewater management system based on the pollutant concentration could not assess environmental risk on aquatic ecosystems since they are not reflective of real toxic effects.[1,2] In this sense, the use of bioassays can provide a direct and appropriate measure of toxicity to complement the physicochemical measures of quality of industrial wastewater.[3]

In addition to the application of bioassay in water quality management system, identification of toxicants plays an important role in wastewater management. In particular, the USEPA offers a method,[4] toxicity identification evaluation (TIE), which describes physical and chemical manipulations that can have an effect on the toxicity. This process helps to develop cost effective treatment system and establish strategies for reducing loads of the toxicant.

Metal plating wastewater contains various

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kinds of dangerous heavy metals and toxicants.[5] However the metal plating industries in Korea have reported difficulties in treatment of wastewater that requires several steps of pH changing and large amount of chemicals since most of them are small businesses.[6] Thus discharges from metal plating industry still show a toxic effect on aquatic organisms though they satisfy the current permit limits. This strongly supports the importance of toxicity identification and reduction evaluation in wastewater treatment systems. Thus, the objectives of this work were to clearly identify the toxicity of metal plating wastewater, and to suggest cost effective wastewater treatment strategies.

METARIALS AND METHODS

Physicochemical Analyses and Toxicity Tests

Metal plating wastewater was grab sampled from an industrial complex in Siheung, Korea, in July 2005. The samples were initially analyzed for pH, COD and Cr(VI). The COD values were determined using a colorimeter (Thermo Orion AQ2040, USA) and test kits (Humas HS-COD, Korea). Cr(VI) was determined with diphenylcarbazide solution by measuring the absorbability at 540 nm. Heavy metals were measured using inductively coupled plasma atomic emission spectrophotometer (ICP-AES, Jobin Yvon, 138 Utrace).

Acute toxicity tests were performed with *Daphnia magna* according to OECD standard procedure.[7] Animals were obtained from the Korea Institute of Toxicology (Daejeon, Korea), and cultivated at 20 ± 2°C with 16 : 8 hr light : dark photoperiod in the M4 medium. Each toxicity test consisted of five dilutions one control with four replicates per treatment. Each test vessel contained 10 m L^{-1} test solution and five animals. Immobilization data was used to calculate EC_{50} (%) by US EPA Probit analysis or Trimmed Spearman-Karber method. Toxicity of metal plate wastewater was evaluated by transforming the EC_{50} value into toxic unit ($TU=100/EC_{50}$).

Toxicity Identification

To identify the toxicants of metal plating wastewater, standard TIE phase I procedure was used.[4,8] The TIE manipulations include graduated pH, solid phase extraction (SPE) and ion exchange (IE) tests. Just before the toxicity identification process, toxicity of unmanipulated wastewater was determined for baseline test. The SPE manipulations were performed using octadecyl C_{18} columns (Discovery, USA). For the IE manipulations, cation and anion exchange columns were prepared with 60 m L^{-1} syringes filled with either cation (Amberlite IR-120H, Aldrich) or anion (Amberlite IR-410, Aldrich) exchange resins.[8] In the case of mixed-bed exchange manipulation, samples were prepared by passing through both the anion and cation exchange columns. Graduated pH manipulation involves pH adjustment of wastewater to 6, 7 and 8 with reagent grade HCl and NaOH, and filtration with GF/B filters (Whatman, USA).

Synthetic wastewater was prepared with AR grade reagents such as K_2CrO_7, $CuCl_2 \cdot 2H_2O$, $Ni(NO_3)_2 \cdot H_2O$, $CaCl_2$, $MgCl_2$, NaCl and KCl, and used to confirm toxicity of metal plating wastewater. The pH of samples was adjusted to initial pH of metal plating wastewater (1.83 ± 0.02). The toxicity data was analyzed with 95% confidence interval Student t-test using SAS 9.1 software. Toxicity tests with various combinations of Cr(VI), Cu and Ni concentrations were also performed to quantitatively evaluate interactions between toxicants.[9] Toxicity tests were triplicate and the results were analyzed by multiple regression with 95% confidential level.

RESULTS AND DISCUSSION

Toxicity Identification

Physicochemical properties and initial toxicity of metal plating wastewater are summarized in Table 1. The wastewater contained high concentration of Cr (298 mg L^{-1}), with most of the chromium in the form of Cr(VI) (280 mg L^{-1}). In addition, Ni (29.5 mg L^{-1}) and Cu (26.5 mg L^{-1}) were included and all these heavy metals

Table 1. Physicochemical properties of metal plating wastewater

pH	COD	Cr (VI)	Cu	Ni	Ca	Mg	24-h TU
1.83	77	280	26.5	29.5	26.3	3.5	435

Concentrations in mg L^{-1} except for pH and TU (toxic unit).

were in levels toxic to *D. magna*. It was found 24-h EC_{50} values for Cr(VI), Cu(II) and Ni(II) were 0.43, 0.39 and 13.45 mg L^{-1}, respectively. Initial TU of metal plating wastewater determined by 24-h acute toxicity test was 435.

Figure 1 shows toxicity reduction of metal plate wastewater by TIE manipulations. Solid phase extraction had no significant effect, suggesting metal plating wastewater toxicity was not caused by organic compounds, particularly non-polar compounds. For ion exchange manipulation, both anion and mixed exchange markedly reduced toxicity. However, toxicity was not changed significantly after cation exchange that removed heavy metals such as copper and nickel. This indicates the toxicity of metal plating wastewater is mainly caused by anions, particularly inorganics. Additional toxicity tests were performed with samples readjusted pH to 6 instead of pHi (1.83) after ion exchange. Toxicity was further decreased by pH adjustment, but, the reduction was much lower than that caused by anion exchange. This suggests pH effect on toxicity of metal plating wastewater is not significant.

As indicated in results of graduated pH manipulation at pH 6, 7 and 8, toxicity of metal plating wastewater was not sensitive to pH change. Generally, anion solubility was relatively insensitive to changes in pH while solubility of cationic metals is dependent on pH value. Around 99% and 80% of Cu and Ni in metal plating wastewater, respectively, were removed by filtration at pH 7. This strongly supports the toxicity of metal plating wastewater is not caused by Cu or Ni, but mainly by Cr(VI).

Toxicity Confirmation

Since Cr(VI) was identified as a main toxic element of metal plating wastewater, synthetic wastewater containing only Cr(VI) (280 mg L^{-1}) was made to confirm the toxicity. As indicated in Figure 2, the synthetic sample (24-h TU = 725) had a very different toxicity comparing with initial toxicity of metal plating wastewater (24-h TU = 435). It seems some elements in the metal plating wastewater can affect the chromium toxicity. Metal plating wastewater contained appreciable amounts of nickel and copper, so several synthetic wastewaters were prepared with combinations of Cr(VI) (280 mg L^{-1}), Cu(II) (26.5mg L^{-1}) and Ni(II) (29.5 mg L^{-1}). Mixture toxicity of Cr + Cu (24-h TU = 417), Cr + Ni (24-h TU = 461) and Cr + Cu + Ni (24-h TU = 476)

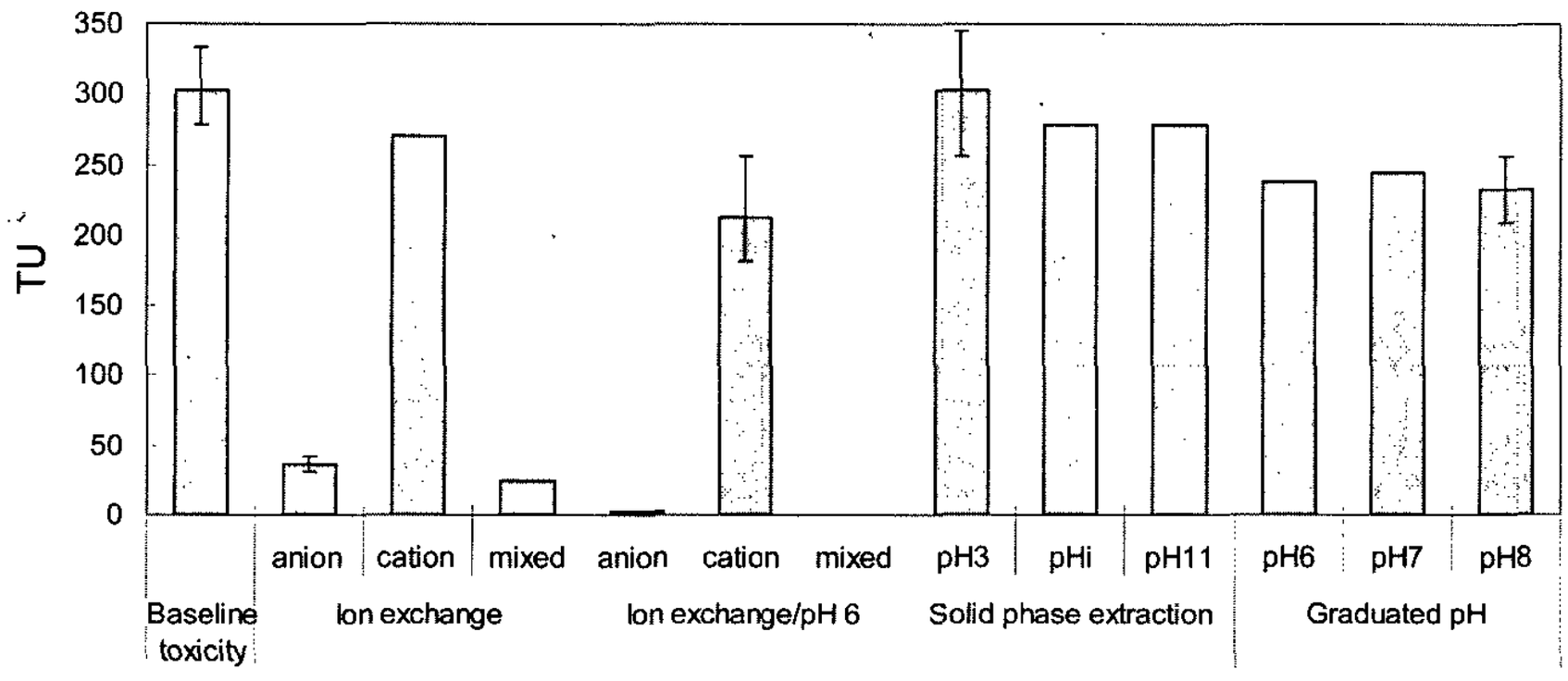

Figure 1. Toxicity reduction of metal plating wastewater by TIE manipulations used in this work. The pHi means initial pH (1.83) of metal plate wastewater.

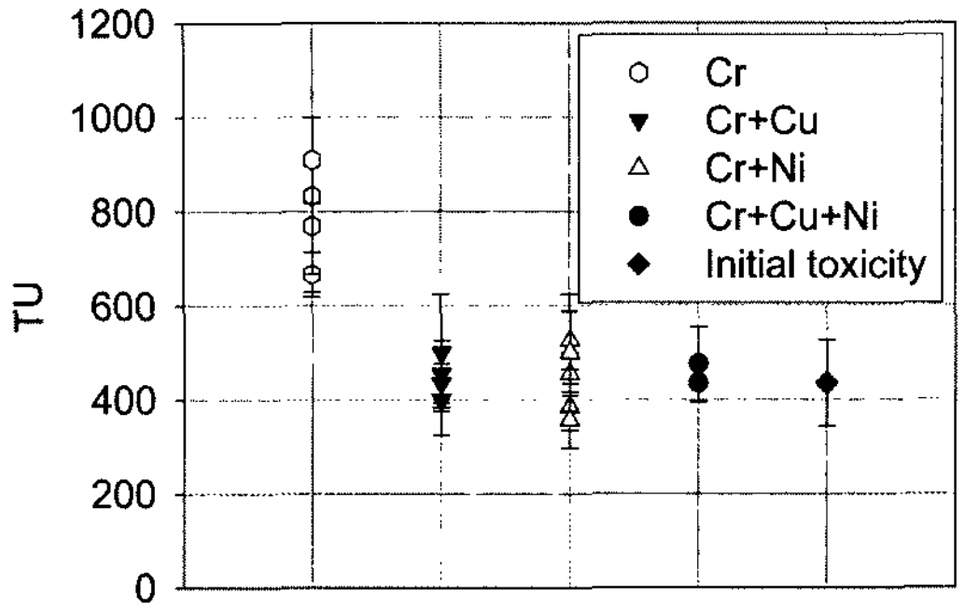

Figure 2. Toxicity confirmation of metal plating wastewater with synthetic wastewater containing Cr(VI) (280mg L^{-1}), Cu(II) (26.5mg L^{-1}) and Ni(II) (29.5 mg L^{-1}).

Table 2. Effect of metal ions (20 mg L^{-1}) addition on chromium toxicity to *D. magna*

Metals	24-h TU	95% confidence interval
none	725	625 - 897 [a]
Ca	515	395 - 746 [a]
Mg	633	575 -709 [a]
K	699	581 - 877 [a]
Ni	461	392 - 559 [b]
Cu	417	350 -518 [b]

showed a significant drop compared with the toxicity of Cr(VI) alone (Figure 2). This suggests copper and nickel might have antagonistic interaction with chromium. However, other cations such as calcium, magnesium and potassium had no significant effect on chromium toxicity (Table 2).

It was found that Cr(VI) induced oxidative damage to DNA by generating reactive oxygen species during its reduction to Cr(III).[10] And Cu had strong effect on induction of enzymes that reduce this oxidative stress.[11] It was also reported that copper and nickel enhanced the chromium tolerance of *D. magna.*[12] Thus the antagonistic interaction between copper and chromium could be explained, however, more investigation should be made to fully understand the interaction between nickel and chromium.

To quantitatively evaluate the antagonistic interaction, fixed concentration of chromium (43.00 mg L^{-1}) was mixed with copper (0.03 - 3.90 mg L^{-1}) and nickel (1.35 - 135.00 mg L^{-1}), and their combined toxicity was determined. There was a significant relationship between combined 24-h TU and concentrations of Cu(II) and Ni(II) (R^2 = 0.76, $p < 0.05$), which is described by the following equation:

$$TU = 3.67 \times \ln([Cu] + [Ni]) + 79.44$$

The above result suggests both copper and nickel negatively affect chromium toxicity by similar level, and this should be further investigated.

CONCLUSION

From the results of toxicity identification process, it is found the toxicity of metal plating wastewater is mainly caused by antagonistic interaction between chromium, nickel and copper. In addition, the interaction can be quantitatively estimated with a simple equation developed in this work. As revealed in this work, anionic species of chromium played an important role on the toxicity of metal plating wastewater. However, in general, anions could not be easily removed through conventional processes such as precipitation. According to the results of this study, anion exchange process effectively removed the chromium. Therefore cation and anion exchange methods could be employed to treat metal plating wastewater containing toxic heavy metals.

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