

Supplementary File

Methodology

1.1. Materials

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, H_2O_2 (30%), tartaric acid, formaldehyde and formic acid were obtained from Wako Chemicals, Japan. Other organic acids such as tartronic acid, glycolic acid, glyoxylic and oxalic acid were obtained from Wako Chemicals, Japan. The actual Cu electroless plating solution was provided by a local plating company.

1.2. OH radical detection during Fenton reaction

Spin trapping/ESR technique was used to detect OH radical formation during Cu- and Fe-Fenton reactions. DMPO, H_2O_2 and either Cu(II) or Fe(II) solutions were combined in a glass tube. Appropriate volume of each prepared reaction sample was transferred to a quartz flat cell and then the ESR spectrum was measured at room temperature using an RE-2X ESR spectrometer (JEOL Ltd.). The hyperfine splitting constant was calibrated using Mn^{2+} as an external standard.

1.3. Fenton treatment of organic acids

The oxidation of individual Cu plating waste components was initially conducted. In this case, 100 mM each of tartaric acid, formaldehyde and formic acid were subjected to Fenton reaction at different pH (3 and 4) and temperature conditions (25°C and 50°C). The amount of Cu^{2+} employed was 20 mM Cu^{2+} . For tartaric acid and formaldehyde, 400 mM of H_2O_2 was utilized while for formic acid, 200 mM was used. Samples were obtained at specific time intervals and then analyzed for residual organic compounds, COD, TOC and H_2O_2 . During

runs with tartaric acid, the formation of bluish white precipitates was observed. Based on the analysis of supernatants at alkaline pH, these were found to be copper oxalate. Hence, it was necessary to increase the solution pH ($\text{pH} > 10$) of the samples for organics analysis so as not to underestimate its oxalic acid content.

The Fenton oxidation of an actual electroless Cu^{2+} plating waste was next considered. In a typical run, the pH was initially adjusted to pH 3 and then H_2O_2 was added batchwise at 407 mM each until a total of 2038 mM. The initial temperature was 25°C . After a reaction time of 5 min per H_2O_2 addition, samples were taken for analysis. The concentrations of COD, TOC, H_2O_2 , formaldehyde as well as organic acids were determined. The pH was maintained at pH 3 all throughout the reaction while the temperature was kept above 50°C . Similar to the above runs with tartaric acid, the samples were also analyzed after base addition to release the oxalic acid from its Cu^{2+} complex.

To evaluate the feasibility of alkaline precipitation of the Cu^{2+} ion, the pH of the treated solution was increased to $\text{pH} > 11$ with 10 M NaOH while the temperature was still above 50°C . The formed flocs were allowed to settle and the sludge volume was determined. The precipitate was then collected and subjected to further analysis by XRD.

For all experiments, duplicate runs were made and the average values were reported.

1.4. Analytical Methods

The metal concentration was determined using the SPS 3000S Inductively Coupled Plasma spectrometer (Seiko Instruments, Japan).

The total organic carbon (TOC) was analyzed by a Shimadzu TOC-500 (Shimadzu Co., Kyoto, Japan). COD was analyzed by the permanganate method according to JIS K1401.

The concentrations of tartaric acid and oxidation metabolites particularly oxalic acid and formic acid were simultaneously evaluated by Capillary electrophoresis and with a Dionex Ion Chromatograph using an ED40 Electrochemical detector.

H₂O₂ analysis was performed using an Agilent 1100 HPLC. A 4.6 x 25 mm Cosmosil monomeric type octadecyl group 5C18-MS-II column containing high purity spherical silica of 5 µm particle size, 12 nm pore size and with endcapping treatment was used (Nacalai, Japan). The mobile phase was 10% methanol (v/v) at 1 mL min⁻¹. The UV detector was set at 254 nm.

Formaldehyde was analyzed by UV-Vis spectrometer after reaction with 4-amino-5-hydrazine-3-mercapto-1,2,4-triazole (AHMT) at alkaline condition. In a typical analysis, diluted sample (<0.1 mM) was combined with similar volumes of 5 N KOH and 0.5% (w/v) AHMT in 0.5 M HCl solution. After 20 min, same volume of 0.75%(w/v) potassium periodate in 1% KOH solution was added. The absorbance of the samples was analyzed at 550 nm.

For characterization of water content of the sludge as well as its composition by XRD, the sample was filtered through 55 mm 5C Advantec filter papers under 0.09 MPa pressure. The wet mass of the sludge was recorded. The sludge was air dried for 3 days under ambient room conditions and the final mass was taken. The percent water content of the sludge was determined. The X-ray diffraction patterns of the dried sludge were also obtained using a RINT 2000 Rigaku X-ray diffractometer (Japan).