

Recovery of Phosphorus from Waste Solution of Electroless Nickel-Phosphorus Plating

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Abstract We attempted to recover phosphorus species from a waste plating solution of electroless nickel-phosphorus plating. With the aim of increasing the recovery yield by oxidizing phosphite to phosphate efficiently, we examined ozonation of a model plating solution by supplying ozone-containing oxygen gas to the solution employing an aerated mixing vessel. As a result of the measurements of the transient changes in the concentrations of the phosphorus species and dissolved ozone in the solution, we confirmed the effect of the organic additives contained in the plating solution on the ozonation efficiency. Calcium chloride was subsequently added to the ozone-treated solution to precipitate the phosphate as calcium hydrogen phosphate, which was poorly soluble to water. At this moment, the recovery yield of the phosphorus from the model waste plating solution was greater than 86%.

1 Introduction

With the progress of economic activities, recovery of valuable resources is becoming more and more important from the viewpoints of both resource management and environmental protection. Although phosphorus is one of the key materials for agricultural and industrial production, depletion of natural phosphorus has been of great concern. Bradford-Hartke *et al.* (2015) reported that, in the period from 1983 to 2013, the global consumption of phosphate increased by 25%, while the price of phosphate rock increased by 133%. In addition to the economical aspect, to prevent eutrophication of water systems, it is essential to control discharging wastewater which contains phosphorus species (Caspers, 1984). Phosphorus has conventionally been recovered or recycled from wastewater by (i) physicochemical methods such as reactive crystallization (Hirasawa *et al.*, 1981a, 1981b, 1981c; Shimamura *et al.*, 2006) and adsorption (Brattebø and Ødegaard, 1986), or by (ii) biological methods such as phostrip process (Szpyrkowicz and Zilio-Grandi, 1995) and anaerobic-oxic process (Tsuzuki, 2007).

Electroless plating is a useful technique which enables to form a metal-plated layer on the surface of metals, ceramics or plastics, without external power supply (Krulik, 1978). Since electroless nickel-phosphorus plating (ENPP) has the advantages in the viewpoints of corrosion resistance and fast deposition rate, it is increasingly applied to the manufacture of automobiles, electronic devices, and precision instruments. Oxidation of sodium hypophosphite, a reducing agent in ENPP to

supply electrons for the reduction of metal ion species in a plating solution, is accompanied by the generation of phosphorus species such as phosphite. Although we expect that reactive crystallization is one of the most efficient methods to recover phosphorus from the waste plating solution, without pre-treatment to oxidize phosphite to phosphate, it is difficult to precipitate phosphorus in a solid form because phosphite salts are soluble to water. Fujita *et al.* (2006) examined wet oxidation of phosphite with the initial concentration of 0.1 mol/L under the varied partial pressure of oxygen in the range of 0.5–5 MPa at 453 K employing a pressure vessel. They reported that the maximal conversion of phosphite to phosphate after the treatment of 180 min was 78% by optimizing the initial pH of the plating solution.

An aerated mixing vessel (AMV) is an efficient and useful apparatus which has been utilized in various chemical processes. Recently, we examined ozonation of aqueous phenol employing an AMV combined with commercial high-silica zeolite pellets (Yamamoto *et al.* 2018). Although AMV is a promising apparatus to enhance dispersion of bubbles in a liquid phase, as far as we have investigated, AMV employing ozone has not yet been applied to treat waste plating solution. In this study, we attempt wet oxidation of phosphite to phosphate in a model plating solution by ozonation employing the AMV. The effect of the presence of organic additives contained in the plating solution on the ozonation efficiency is examined and discussed. After phosphite is completely oxidized to phosphate, we also examined the recovery of phosphate as precipitation of the calcium salt to discuss the recovery yield.

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2 Experimental

2.1 Preparation of model waste plating solution

Table 1 shows the typical composition of the waste plating solution from ENPP process. Sodium succinate hexahydrate, DL-malic acid and sodium saccharin dehydrate are the organic additives to the plating solution as a buffering agent, a complexing agent and a brightener, respectively. 0.30 L of the original plating solution was diluted 10 times to prepare 3.0 L of the model plating solution, which was set to the vessel prior to ozonation. For the comparison, ozonation of an aqueous solution which contained only sodium phosphinate with the same concentration as the model waste plating solution was also examined.

Table 1. The composition of the original waste plating solution

| Chemical species | Molar concentration [mol/L] |
|--------------------------------|-----------------------------|
| Sodium succinate hexahydrate | 0.10 |
| DL - Malic acid | 0.10 |
| Nickel(II) sulfate hexahydrate | 0.10 |
| Sodium phosphinate monohydrate | 0.30 |
| Sodium saccharin dihydrate | 0.0060 |

2.2 Ozonation of waste plating solution

Figure 1 shows a schematic image of the experimental setup employed for ozonation in this study. The ozone generator was a dielectric-barrier discharge type (SO-O3UN-OX), which we purchased from Hamanetsu Corp. Oxygen gas (G3 grade) was supplied to the ozone generator as the feedstock of ozone at a constant flow rate

of 0.50 L/min. The gas from the outlet of the ozone generator was then introduced to the AMV as bubbles through a Shirasu-Porous-Glass (SPG) hollow membrane with the average pore size of 5 μm , which we purchased from the SPG Technology Co., Ltd. The SPG membrane was placed at the centre of the vessel and at the height of 30 mm from the bottom. The inner diameter, the depth and the capacity of the vessel were 130 mm, 200 mm and 4.0 L, respectively. During ozonation, the solution was agitated using a magnetic stirrer at a constant stirring rate of 600 rpm. The temperature of the vessel during ozonation was kept at 298 K. The gas from the outlet of the vessel was introduced to the activated carbon bed for degrading ozone and was then released into the atmosphere.

2.3 Recovery of phosphate from waste plating solution after ozonation

After ozonation, we adjusted the pH of the solution to 10 and then added calcium chloride solid to the solution at 283 K. The molar ratio between calcium chloride to phosphate was fixed to 1.0. Since the solubility of calcium chloride to water was greater than 6.0×10^2 g/L at 283 K, the added calcium chloride could be easily dissolved to the solution. After the addition of calcium chloride, the solution was filtered to collect the precipitation of calcium hydrogen phosphate dispersed in the solution. We determined the recovery yield of the phosphorus species based on the concentration of phosphate remained in the filtered solution. Finally, the collected solid containing calcium hydrogen phosphate was dehydrated at 413 K for 60 min.

2.4 Analytical methods

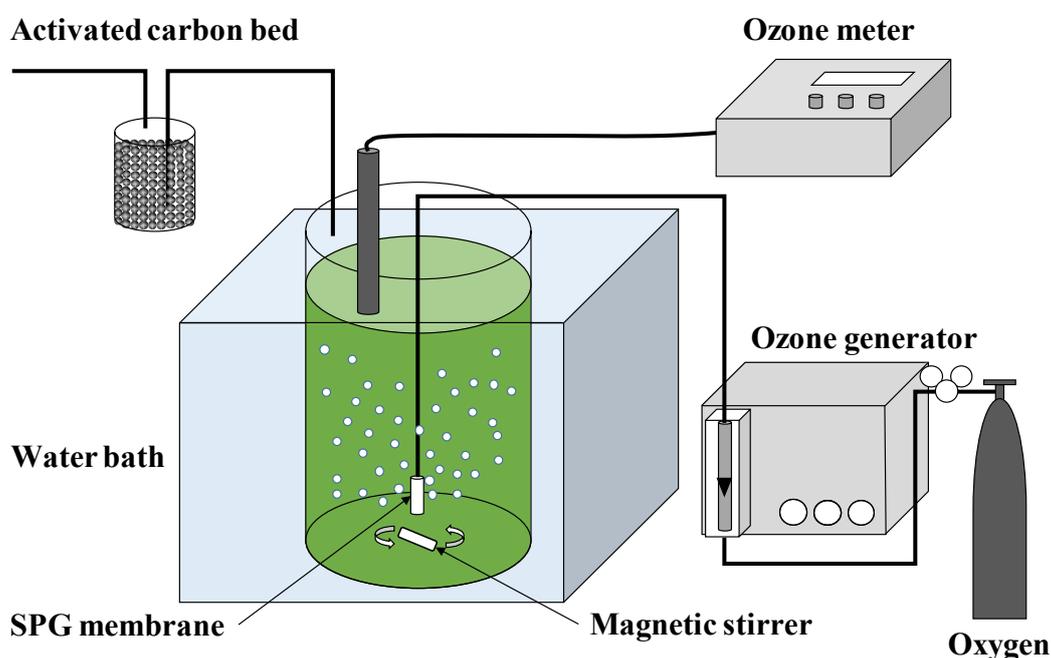


Figure 1. Experimental setup for ozonation.

2.4.1 Concentration of dissolved ozone

While ozone was being supplied to the vessel, the transient change in the concentration of ozone dissolved in the solution was measured using an ozone meter (OZ-20, DKK-TOA Corp.) based on the diaphragm polarographic method.

2.4.2 Concentration of phosphorus species

During ozonation, the concentrations of the phosphorus species (phosphite and phosphate) in the solution was measured by sampling the solution at a certain time interval. The sample was analysed employing a high-performance liquid chromatograph (HPLC) system equipped with a conductivity detector (IA-100, DKK-TOA Corp.) As the eluent, 2.5 mM of phthalic acid was supplied to the column (PCI-311S, DKK-TOA Corp.) at the flow rate of 1.5 mL/min. To determine the concentration, the peak area of the HPLC chromatogram was analysed based on the calibration curves, which we measured using disodium hydrogen phosphite (Na_2HPO_3) and dipotassium hydrogen phosphate (K_2HPO_4) as the standards, respectively.

2.4.3 Concentration of total organic carbon (TOC)

The transient change in the TOC concentration during ozonation of the model plating solution was measured employing a TOC analyser (TOC-V_{CPH}, Shimadzu Corp.) by sampling the solution at a certain time interval. Potassium hydrogen phthalate aqueous solution with the concentration of 1000 mg/L was prepared and used as the standard for calibration.

3 Results and Discussion

3.1 Oxidation of phosphite to phosphate

Figure 2 shows the transient change of the chromatograms obtained by the measurements of sodium phosphinate solution and model waste plating solution, respectively. We have confirmed that the positive peaks detected at the retention time of 6–8 min and 9–11 min correspond to phosphate and phosphite, respectively. The transient changes in the concentrations of phosphorus species, which are calculated based on the peak area in the chromatogram, and dissolved ozone are compared in Figure 3. In the case of ozonation of sodium phosphinate solution as indicated by blue symbol, it can be seen that phosphite is almost oxidized to phosphate in less than 40 min. Concentration of dissolved ozone is found to increase rapidly after oxidation of phosphite to phosphate is completed. On the other hand, in the case of ozonation of the model plating solution as indicated by red symbol, it takes approximately 300 min to oxidize phosphite to phosphate completely. It is found that the concentration of ozone gradually increases when phosphite is almost oxidized to phosphate. This is because dissolved ozone is partially consumed to oxidize the organic additives as summarized in Table 1.

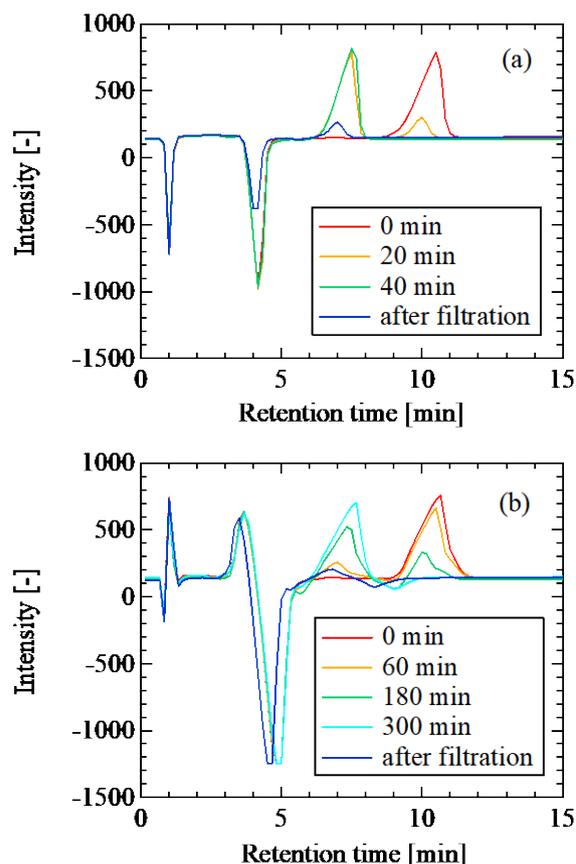


Figure 2. Chromatograms obtained by the measurements of (a) sodium phosphinate solution and (b) model waste plating solution

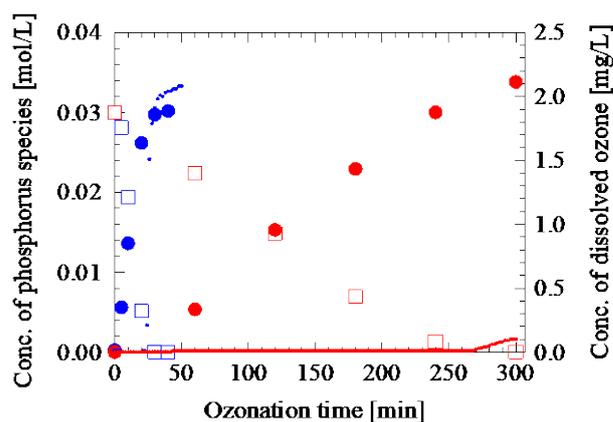


Figure 3. Transient change in the concentration of phosphorus species (open square: phosphite, closed circle: phosphate) and dissolved ozone (dot) during ozonation of sodium phosphinate solution (blue symbol) and model waste plating solution (red symbol)

As shown in Figure 4, the TOC measurement revealed that the TOC concentration after the ozonation for 300 min slightly decreased as compared with the initial concentration. The result indicates that most organic additives in the plating solution remain undegraded although phosphite is almost converted to phosphate, and that dissolved ozone is still consumed for oxidizing the organic additives. Thus, in the presence of the organic

additives, the ozonation efficiency to oxidize phosphite to phosphate is confirmed to decrease. To increase the efficiency, we plan to modify the dispersion condition of ozone which will be examined in the subsequent study.

3.2 Recovery yield of phosphorus species

Figure 5 shows the distribution diagram of phosphate, which are calculated from the acid constants of $pK_{a1}=2.12$, $pK_{a2}=7.21$ and $pK_{a3}=12.67$, respectively. Based on the diagram, we determined the optimal pH as 10 for the recovery of phosphate by precipitating as calcium hydrogen phosphate. Because of the small solubility (0.02g to 100 g of water at 298 K) of calcium hydrogen phosphate, the aqueous solution became turbid as a result of the precipitation immediately after the addition of calcium chloride to the solution. As can be confirmed from Figure 2, it is found that a small amount of phosphate still dissolves in the solution even after precipitated calcium hydrogen phosphate is removed by filtration. Since the concentration of the phosphate remained in the solution is 0.040 mol/L, we estimate the recovery yield of phosphate from the solution as 86.7%. We expect that further cooling of the solution or addition of anti-solvent (alcohol) before filtration will decrease the concentration of the residual phosphate in the solution and increase the recovery yield.

4 Conclusion

In this study, we examined recovery of phosphorus species from a model waste plating solution as the calcium salt employing an AMV. We confirmed that ozonation of the plating solution could steadily oxidize phosphite to phosphate in the solution, although the ozonation efficiency decreased as a result of partial consumption of dissolved ozone by the reaction with the organic additives contained in the solution. By adding calcium chloride to the ozone-treated solution, phosphate could be successfully recovered as precipitation of the calcium salt with the yield of greater than 86%. To further increase the recovery yield, modification of the ozone-supplying method to the AMV will be examined in the subsequent study.

Acknowledgment

This work was supported by the Hyogo Science and Technology Association.

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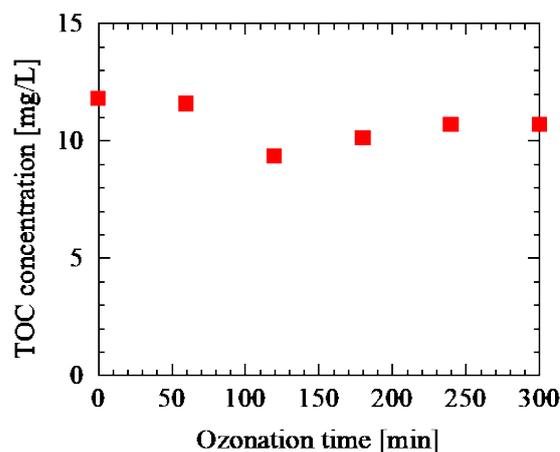


Figure 4. Transient change in the TOC concentration during ozonation of model waste plating solution

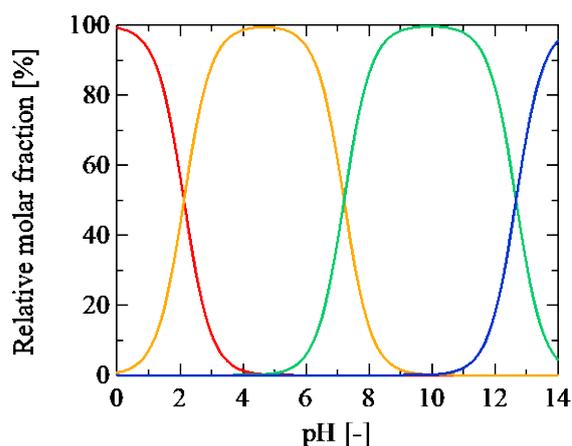


Figure 5. Relation between pH and relative molar fraction of phosphate in water at 298 K; red: H₃PO₄, yellow: H₂PO₄⁻, green: HPO₄²⁻, blue: PO₄³⁻

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