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Feasibility study of UV-Fenton and chemical precipitation process for the recycling of spent electroless nickel plating baths

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ABSTRACT

The advanced oxidation technology using UV irradiation and addition of hydrogen peroxide and catalysts, UV-Fenton, is effectively tuned specifically to oxidize phosphite and hypophosphite into phosphate which can then be readily precipitated by dosing iron salt. After 20-hour UV-Fenton process, 93% COD is removed and 91% of phosphite and hypophosphite mixture can be oxidized into phosphate. Total phosphorus concentration in effluent water decreases to 14.3 from 19,350 mg/L after entire processes.

1. INTRODUCTION

The electroless nickel (EN) plating is important one of the surface treatment methods because the advantages of EN include uniformity, corrosion resistance, lubricity and desirable electrical properties. The EN plating process is simple and it does not use external electric current to produce deposit. EN plating reaction is as follows:

$$3NaH_2PO_2 + 3H_2O + NiSO_4 \rightarrow 3NaH_2PO_3 + H_2SO_4 + 2H_2 + Ni \quad (1)$$

With the time, nickel ion is simultaneously reduced to deposit of surface and the spent plating bath is discarded to maintain plating quality. The spent EN bath still contained high concentration of organic and phosphorus compounds.

Considering the limited landfill space and recent high nickel prices, it is urgent to develop a reduced sludge generation and effective nickel recycling technique to treat the spent plating baths. The advanced oxidation technology using UV irradiation and addition of hydrogen peroxide and catalysts is a well recognized technique able to oxidize a very large variety of organic and inorganic compounds present in wastes, and here specifically to oxidize phosphite and hypophosphite into phosphate which can then be precipitated readily by following chemical precipitation processes. In the process, hydroxyl radical, as a strong oxidant (E^0 = 2.8 V), is efficiently produced and can effectively decompose waste compounds.

In this study, we report the feasibility study of recycling process of spent electroless nickel plating baths in terms of waste reduction as well as reuse of water.

2. EXPERIMENT DETAILS

The UV-Fenton process is designed as shown in Fig. 1. The photo-reactor has a total volume capacity of 20 liters. The UV irradiation is provided by two low-pressure mercury lamps with UV intensity at 254nm (125W and 500W, respectively). The spent EN plating solution is mixed and circulated using a pump. Table 1 shows the basic property of EN plating solution. It contains 19,350 mg/L total phosphorus, 23,520 mg/L COD and 4,736 mg/L nickel ions, respectively.

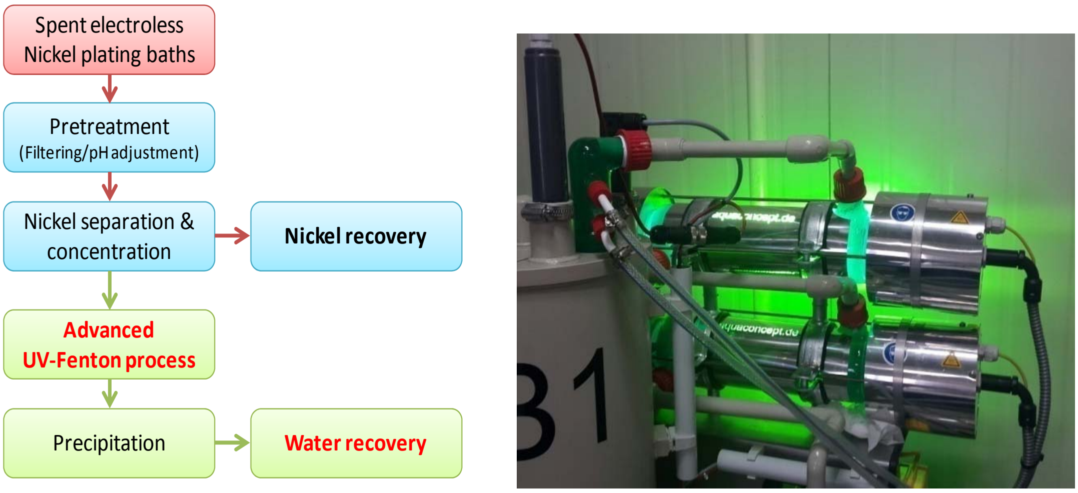

Fig. 1 Schematic diagram for treatment of spent electroless Nickel plating baths (left) and advanced UV-Fenton process (right), respectively.

Table 1 Characteristics of the spent electroless Ni plating bath

Parameters	Value
pH	4.0
Chemical oxygen demand (mg/L)	23,520
Total phosphorus (mg/L)	19,350
Nickel (mg/L)	4,736

3. REMOVAL EFFICIENCY OF COD AND PHOSPHORUS COMPOUNDS

The experiment conditions are represented in Table 2. At first, the pH of the sample was adjusted to 2.0 with HCl. And calculated amount of Fe^{3+} salt was added to the photo-reactor as a catalyst. The H_2O_2 initial addition was 1,000 mg/L and re-added to compensate and sustain certain level of concentration.

The UV-Fenton processes were carried out for spent EN baths, and the results are shown in Fig. 2 and Fig. 3. The Fig. 2 is removal efficiency of COD. After 20 hours of reaction, 93% of initial COD was effectively reduced. Reproducibility was confirmed as shown in Fig. 2. Also, conversion of phosphite and hypophosphite into phosphate in sample were calculated to be above 91% after 20 hours reaction.

Table 2 Experimental conditions for UV-Fenton reaction

Parameters	Value
pH	2.0
UV lamp (nm)	254
Total bath capacity (L)	20
H_2O_2 addition (mg/L)[1)]	1,000
Fe^{3+} (40%) addition (ml/L)	0.2

1) H_2O_2 was re-added in the same concentration, when residual H_2O_2 concentration decreased below 5 mg/L.

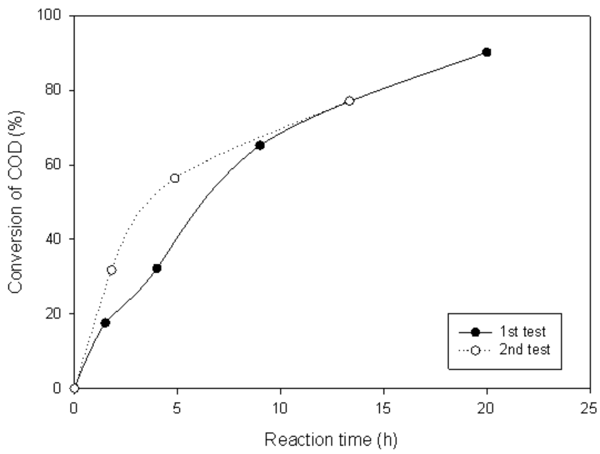

Fig. 2 Removal efficiency of the COD. Experimental conditions: H_2O_2: 1000mg/L, feeding mode: re-addition as residual $H_2O_2 \leq 0.5$mg/L.

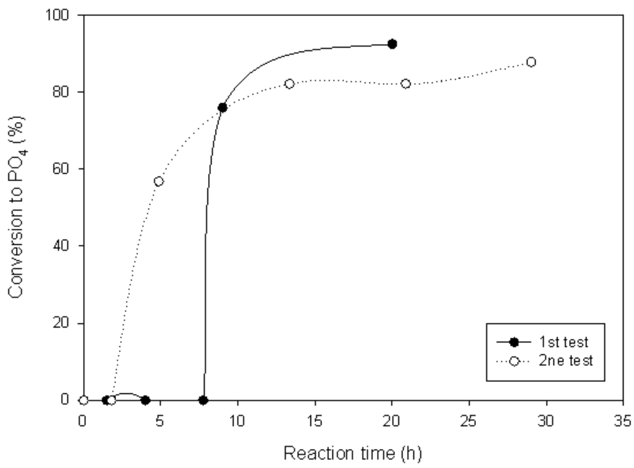

Fig. 3 Oxidation efficiency of the phosphite and hypophosphite into phosphate.

After AOP reaction, phosphate precipitation with Fe^{3+} salt was followed. The pH value was controlled 4.5 with NaOH. The precipitation process is as follows:

$$Fe^{3+} + PO_4^{3-} \rightarrow FePO_4 \qquad (2)$$

Table 3 shows the result of PO_4 precipitation process. After test, total phosphorus concentration was decreased to 14.3 mg/L. The precipitate contains Fe, Ni and P.

Table 3 Result of phosphate precipitation process

	Content	Result (mg/L)
Supernatant	PO_4^{3-}	4.0
	Total phosphorus	14.3
Precipitate	Content	Result (wt%)
	Fe	40.70
	Ni	32.52
	P	14.67
	Cl	7.11

4. CONCLUSIONS

The UV-Fenton process was successfully applied for the recycling of spent electroless nickel plating baths. The initial operating conditions were pH 2.0, 1,000 mg/L H_2O_2 (continuous addition) and 0.2 ml/L $FeCl_3$ (40%). After 20 hours reaction, 93% of COD was reduced and 91% of phosphite and hypophosphite mixture was oxidized into phosphate. Total phosphorus concentration in effluent water was decreased to 14.3 from 19,350 mg/L after entire processes, making sure that the water can be recycled. For a early commercialization of this technology, more detailed assessment is needed since the use of chemicals should be minimized in terms of environmental and economic concerns. Therefore, the introduction of photocatalysts will be considered in the near future.

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