

Integrating multi-method approaches for the green separation and retrieval of nickel and phosphorus from spent electroless nickel plating solutions

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S1 Experimental procedures

100 mL ENP wastewater was put into a 250 mL beaker. A certain amount of NaOH and PMS was added to the wastewater, heated and stirred continuously, and filtered after the reaction for a period of time. The nickel ions, phosphorous and phosphite in the filtrate were measured, and the removal efficiency of nickel ions, and the conversion efficiency of hypophosphate and phosphite to phosphate were evaluated as the following equation 1:

$$A_e = \frac{C_0 - C_e}{C_0} \times 100\% \quad (\text{S1})$$

Where C_0 (mg/L) and C_e (mg/L) correspond to the initial and residual Ni^{2+} ion concentration, or hypophosphate and phosphite concentration. A_e refers to the removal efficiency or conversion efficiency (%).

After the separation of nickel, the pH of the filtrate was adjusted with 10% dilute

hydrochloric acid, and then a certain amount of calcium chloride was added, heated and stirred continuously for a period of time. After filtration, the content of total phosphorus (TP) in the filtrate was determined, and the removal efficiency of TP was calculated according to equation (1).

In the present experiment, nickel was detected by inductively coupled plasma-optical emission spectroscopy (ICP-OES, 7000 Series, ThermoFisher Scientific), and hypophosphite (H_2PO_2^-) and phosphite (HPO_3^{2-}) were analyzed by titration, TP concentrations were measured based on blue molybdenum¹ via UV-Vis spectrophotometer. All experiments were performed three times to minimize error, and the error bar in the data graph refers to the standard deviation (SD).

S2 The preparation of the Activated Carbon Fiber (ACF) electrode and electrochemical experiment

Activated carbon fiber was obtained from Hexcel (Tianjin) Composite Materials Co., LTD, and used as electrode. The ACF with a thickness of 2 mm was cut into 6 cm × 8 cm squares, then thoroughly washed with deionized water, and tested with TDS pen until the number was less than 2 mg/L. It was dried overnight in the oven at 105 °C and stored in an airtight bag for further use. The electrode size was 6.0 cm × 8.0 cm × 0.2 cm, and was fixed on the titanium plate by double-sided conductive adhesive, the electrode spacing was 1.0 cm.

Through using an electrochemical workstation (CHI660D Chenhua Instruments Co., China), the electrochemical performance of the ACF electrodes was investigated by cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS).

These measurements were performed in a three-electrode system in which the working electrode was the ACF electrode. A platinum electrode was used as the counter electrode, and Ag/AgCl electrode was used as the reference electrode. The electrolyte was prepared from low concentration ENP solution. The CV curves were tested at scanning rate of 10 mV/s in the range of $-0.5\text{ V}\sim 0.5\text{ V}$.

S3 CDI measurement

The laboratory-scale CDI device with a three-electrode system was displayed in **Fig. 1(b)**, including a self-made CDI battery, a constant-current voltage regulator power supply, a peristaltic pump and a conductivity meter. CDI battery is made of acrylic plate ($12.0\text{ cm} \times 12.0\text{ cm} \times 0.78\text{ cm}$), titanium plate ($12.0\text{ cm} \times 12.0\text{ cm} \times 0.1\text{ cm}$) and silicone pad. The specific capacitance (C , F/g) of samples can be calculated through the CV curves based on the following equation 2:

$$C = \int idV/(\Delta Vmv) \quad (\text{S2})$$

Where i (A), m (g), ΔV (V), and v (V/s) represent the current, the mass of ACF electrode, the voltage window, and scan rate, respectively.

All experiments were carried out under constant pressure, and the ACF mass consumed was 1.500 g. The initial experiment was based on the ENP solution of 10.91 mg/L Ni^{2+} and 12.29 mg/L TP(P), and 100 mL ENP solution was transported into the CDI battery at a flow rate of 20 mL/min through the peristaltic pump. The change of the conductivity of the solution is monitored with a conductivity meter to determine whether saturation adsorption is achieved. The applied voltage was selected in the range of 0.8 V to 1.6 V. The flow rate of 10 mL/min \sim 50 mL/min was studied under the

optimized voltage. 1M H₂SO₄ or NaOH was used to adjust the pH of the ENP solution to probe the effect of solution pH. The effect of electrode spacing on the deion performance was determined by changing the electrode spacing from 0.5 cm to 4 cm. After the optimum process conditions were determined, the reusable performance of the electrode material was studied by cyclic experiments. After each experiment, the solution was collected and the concentrations of Ni²⁺ and TP in the solution were determined by ICP and UV–Vis spectrophotometer, respectively.

1. Liu, P, Li, C, Liang, X, Lu, G, Xu and J, *Green Chemistry*, 2014.