



# A novel pyridine based polymer for highly efficient separation of nickel from high-acidity and high-concentration cobalt solutions

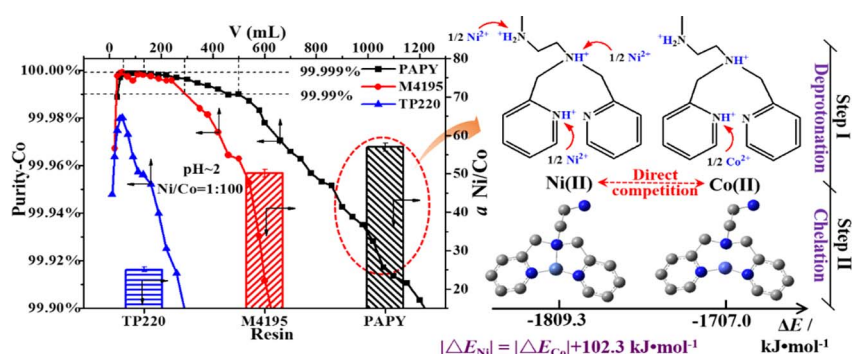


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## GRAPHICAL ABSTRACT



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## ABSTRACT

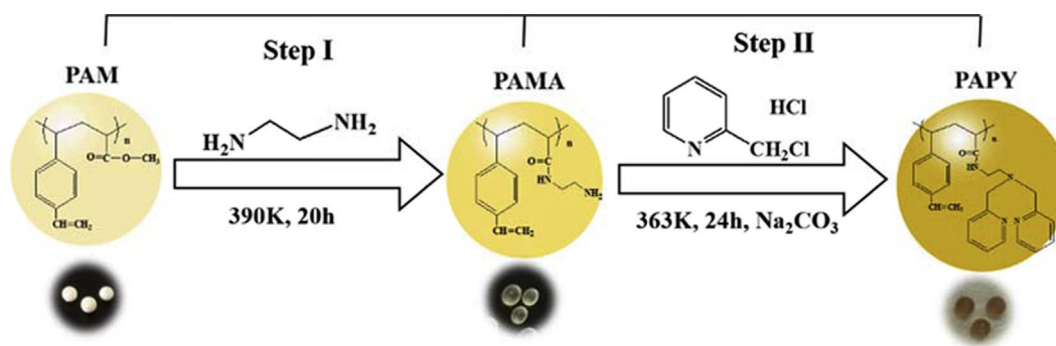
A novel pyridine based polymer (PAPY) bearing typical bis(2-pyridylmethyl)amine and additional amino groups was newly prepared with much lower cost (46.5 USD/kg) than commercial resins with bis(2-pyridylmethyl)amine functional groups such as M4195 and TP220 (134.6 USD/kg). PAPY is a weakly basic resin with poly-methacrylate–divinylbenzene matrix. Due to the relatively more hydrophilic matrix and more modified functional groups, PAPY owned the highest selectivity for nickel from high-concentration cobalt solutions even under highly acidic condition (pH ~ 2). The highest separation factor of 129.2 ( $C_{0, Ni}/C_{0, Co} = 1:5000$ ) could be achieved for Ni(II) versus Co(II) with PAPY, which is 100.1%, 53.6% more than those with M4195 and TP220, respectively. Because of the stronger deprotonation ability and the higher chelation binding energy, Ni(II) could form the more stable structure of two five-member rings in solid phase than Co(II). This may be the predominant mechanisms for the highly efficient separation between Ni(II) and Co(II). More attractively, Co(II) could speed up the initial adsorption rate of Ni(II) by 16.30% due to the affinity of functional groups and the electrostatic repulsion of Co(II). Far more high-purity cobalt (> 99.99%) could be obtained by PAPY in the dynamic tests. With good regeneration and reusability, PAPY possesses great potential in the green and economical preparation of high-purity cobalt.

## 1. Introduction

Due to the characteristics of corrosion resistance, oxidation

resistance, high strength and good ductility, high-purity cobalt with 99.99% or higher purity level is urgently demanded as the target material of superalloys [1], high-quality catalysts [2], magnetic materials

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Scheme 1. Synthetic route of the new pyridine polymer synthesis.

and advanced electronic components [3,4]. However, cobalt and nickel are concomitant metal elements and usually symbiotic or associated in deposit [5]. Thus, it is extremely difficult to obtain pure cobalt or nickel because of their similar physicochemical properties, such as electronegativity, atomic radius, and “hardness” according to the Soft-Hard Acid-Base theory [6]. With the ever-increasing need, various methods, such as solid-phase extraction [7,8], solvent extraction [5,9,10], supported liquid membranes [11,12], and electrodialysis [13] have been developed for the purification of cobalt. Solvent extraction is the most common technique, but uses large quantities of organic solvents resulting in environmental pollution [14]. Conversely, solid-phase extraction has attracted considerable attention, especially for materials containing chelating ligands, endowed with high efficiency and rapid development for the removal of low concentration impurity metals [15–17]. Recently, much attention has been paid to selective recovery of cobalt by acid leaching [18,19]. The acid leach liquor of cobalt is strongly acidic and contains trace impurities of nickel. In order to reduce the consumption of chemical agent, developing a novel chelating polymer to efficiently separate nickel from cobalt from highly acidic solutions is of high importance.

The bis(2-pyridylmethyl)amine functional group has three chelating nitrogen donor atoms from weak-base pyridine and tertiary amine functional groups. Due to the electron withdrawing effect of the aromatic group, the  $pK_a$  values are quite low and one nitrogen atom remains deprotonated in the sulfate solutions even at pH of 1.5. To the best of our knowledge, DOWEX M 4195 (M4195) and Lewatit® MonoPlus TP 220 (TP220) are the representative commercial pyridine chelating resins with the macroporous structure, based on polystyrene-divinylbenzene copolymer, and have been widely applied in the separation of nickel from cobalt solutions [20]. Under strong acidic conditions, heavy metal ions could be removed from aqueous solutions consistent with the following selectivity series:  $\text{Cu(II)} > \text{Ni(II)} > \text{Co(II)}$  [21–23]. However, chloro-methyl ether as a reactant in the reaction of chloromethylated styrene-divinylbenzene copolymer is poisonous and has toxic effects to the environment [24]. Additionally, its utilization rate of functional groups is relatively low (about 20%) and the modification reagent of bis(2-pyridylmethyl)amine is pretty expensive (20989.5 USD/kg), limiting the application in practical engineering. Therefore, it is of great significance to develop a green material carrying more effective functional groups.

As our earlier reported, the polyamine chelating resin NDC-984 can be used for the selective separation of nickel from cobalt with high capacity and good selectivity, but it is poorly resistant to acid [16]. Due to the stronger hydrophilicity and more grafted sites, methacrylate–divinylbenzene copolymers stand out from the rest [25]. Besides, ethylenediamine (EDA, 2.2 USD/kg) and 2-(chloromethyl)pyridine hydrochloride (CPHC, 3238.4 USD/kg) are cheap raw reagents and can be readily used for the preparation of typical bis(2-pyridylmethyl)amine and the additional amino groups. It is inferred that the additional amino group may add the active sites for chelation with the dominant component. As a result, it has remarkable environmental and economic

benefits to successfully graft EDA and CPHC onto poly-methacrylate–divinylbenzene matrix by two steps.

This research was to synthesize the novel pyridine based polymer (PAPY) by a two-step method and compare its ability of purifying cobalt with M4195 or TP220 from acidic streams. In this work, great effort was devoted to investigate the selective separation between Ni(II) and Co(II) in sole, binary and preloading systems by carrying out batch static and column dynamic tests. The inner mechanisms of the exclusive removal of Ni(II) versus Co(II) onto PAPY were further explored using Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectrometry (XPS) and Density functional theory (DFT).

## 2. Materials and methods

### 2.1. Materials

Acrylic polystyrene (PAM) was obtained from Jiangsu Nanjing University Environment Technology Co., Ltd. (Nanjing, P.R. China). DOWEX M 4195 (M4195) was manufactured by Dow Chemical (Midland, USA), and purchased from Supelco-Sigma Aldrich Division (Bellefonte, USA). Lewatit® MonoPlus TP 220 (TP220) was obtained from Lanxess Energizing Chemistry (Cologne, Germany). Cobalt sulfate, nickel sulfate and all other chemical reagents used in the experiments were of analytical grade, and purchased from Nanjing Chemical Reagent Co., Ltd. (Nanjing, P.R. China). Ultrapure water was used throughout this study. The metal ions in aqueous phase were measured using inductively coupled plasma optical emission spectrometry method (iCAP 6000 ICP-OES, THERMO, USA)

### 2.2. Preparation of the novel pyridine polymer PAPY

The schematic illustration of fabricating the newly-synthesized pyridine chelating resin is depicted in Scheme 1, including the morphologies and structures of PAM, PAMA, PAPY. It consists of the following steps: (1) 15.0 g PAM were swelled in a 500 mL three-neck flask by immersing the resin beads into 150 mL polyamine reagent (EDA) for 24 h. Then the reaction was carried out through reflux condensing at 390 K under continuous stirring for 20 h. After being filtered, the resin beads were rinsed with ultrapure water, ethanol and ultrapure water in sequence to remove unreacted agents, and stored in ultrapure water. The obtained polyamine resin was named as PAMA. (2) The obtained PAMA resin, appropriate amount of 2-(chloromethyl)pyridine hydrochloride (dissolved in ethanol) and sodium carbonate were introduced into a 500 mL three-neck flask. The reaction was carried out through reflux condensing at 363 K under continuous stirring for 24 h. After being filtered, the resin beads were rinsed with ethanol, dilute nitric acid and ultrapure water, successively, and then vacuum-dried at 323 K until reaching constant weight. The resin obtained was named as PAPY, and the structural differences with the commercial pyridine chelating resins M4195/TP220 are shown in Table 1.

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