Cobalt and Phosphorous Recovery from Semiconductor Wastewater through Homogeneous Crystallization of Cobalt Phosphate in a Fluidized-bed Reactor

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Abstract
Semiconductor manufacturing involves distinct processes that generate complex wastewater streams that require treatment before it proceeds to the main wastewater effluents. The present study utilized fluidized-bed crystallization to recover resources from the combined synthetic wastewater of chemical-mechanical polishing and etching processes. The study aims to determine the operational conditions to achieve optimum recovery and removal. Maximum removal and granulation of ~99.0% and 96.07% were realized at pH_i range of 7.75 – 8.0 and $[PO_4^{3-}]/[Co^{2+}]$ ratio of 2.0, respectively. Phosphate concentration in etching stream was reduced from 14.0 mM to $[PO_4^{3-}]_d$ of 1.02 mM at optimal conditions. Uniform crystal size of 0.7 mm dimater was attained at hydraulic rentention time of 15 min, upflow velocity 34.38 – 40.11 m h^{-1} and surface loadings of 1.18 kg Co^{2+} m^{-2} h^{-1}. The granules recovered were cobalt phosphate octahydrate mineral $Co_3(PO_4)_2.8H_2O$ as main products as analyzed through XRD analysis. Moreover, SEM-EDS analysis showed ~34.0% Co, ~21.0% P and ~45.0% O having a petal-like structure.
Keywords: Resource recovery, cobalt phosphate, fluidized bed reactor, homogenous crystallization, semiconductor wastewater

1. Introduction

Semiconductor manufacturing involves distinct processes that generate complex wastewater streams that require treatment before it proceeds to the main wastewater effluents. Integration of resource recovery and economical treatment that may lead to a green and sustainable production process. Morever, characterization of wastewater by its composition such as heavy metals, inorganic acids and organic species is important to effectively design zero-waste treatment process.
Resource recovery using fluidized-bed crystallization (FBC) have been utilized by various industries instead of conventional chemical precipitation that only generates unusable waste sludge. FBC enhances the crystal growth with the support of seeds (active sites). Previous studies had demonstrated the effectivity of FBC process to recover valuable products such as metal carbonates (Chen et al., 2015), struvite (Kozik et al., 2014), and iron salts (Priambodo et al., 2017). Conventional FBC process generates impure solid granules due to the inclusion of seeds (e.g. silica sand) that reduces its economic value (Ballesteros et al., 2016). To address this, a novel fluidized-bed homogeneous crystallization (FBHC) method was introduced to synthesize high-purity granules with high market value. In this study, FBHC was utilized to recover resources from the combined synthetic wastewater of chemical-mechanical polishing CMP (cobalt-rich stream) and etching process (phosphate-rich stream). The study determines the operational conditions to achieve optimum recovery and removal.

2. Experimental Methods

$Co_3(PO_4)_2.6H_2O$ (>98% purity) and $NaHPO_4$ ((>98% purity) were prepared as separate synthetic wastewater solution. pH_e was adjusted with 1.0 M HNO_3 and/or NaOH solution. All the reagents are analytical grade and RO water (18.2 MΩ cm) was used in solution preparation.
A 450 mL cylindrical glass column laboratory scale fluidized-bed reactor (FBR) set up with two parts was used for this experiment: a lower and expansion column which has a 2 cm inner diameter with a height of 80 cm and 4 cm with 20 cm, respectively. At the bottom of the reactor are two feeding inlets dispensing the cobalt and phosphate wastewater. The solution was continuously recirculated at constant reflux rate using a peristaltic pump. Sampling and pH monitoring were conducted from the effluent at the upper column. Initial run involved varying the aquatic parameters as listed in *Table 1* while keeping hydraulic loading conditions constant. Both wastewater streams had the same influent flow rates of $Q_{Co} = Q_P = 15$ mL min^{-1} resulting to a hydraulic retention time (HRT) of 15 mins and a constant reflux flow rate of 150 mL min^{-1}.

Homogeneous nucleation was achieved by reacting 7 mM cobalt ions with the precipitant at $[PO_4^{-3}]/[Co^{2+}]$ ratio of 1.5 resulting to a turbid-pinkish solution. The solution was then maintained in a supersaturation state to increase fine formation and ensure crystal growth. Both aquatic conditions and hydraulic parameters were adjusted accordingly to determine the optimum operating condition based on the observed maximum granulation.

Table 1. *Operational conditions in FBHC process*

Aquatic Parameters		Conditions
pH_i	5.0 – 11.0	$[PO_4^{-3}]/[Co^{2+}] = 1.5$
$[PO_4^{-3}]/[Co^{2+}]$	0.5 – 10.0	Optimum pH_i
Hydraulic Parameters		
Q_R (mL min^{-1})	60, 120, 150, 180, 210	Optimum pH_i $[PO_4^{-3}]/[Co^{2+}]$
$Q_T = Q_{Co} + Q_{PO}$ (mL min^{-1})	20, 30, 40, 50, 60, 90, 120	Optimum pH_i $[PO_4^{-3}]/[Co^{2+}]$

Effluent samples gathered from the reactor were analyzed using atomic absorption spectrophotometer. The generated granules formed in the reactor were analyzed using x-ray diffraction (XRD), energy dispersive spectroscopy (EDS) and scanning electron microscopy (SEM). The effectiveness of FBHC process will be determined by two equation: percentage removal (%R) and granulation (%G) as shown in *Eq 1* and *Eq 2*.

$$\%R = \frac{[Co^{2+}]_{in} - [Co^{2+}]_{d}}{[Co^{2+}]_{in}} \quad \text{Eq 1}$$

$$\%G = \frac{[Co^{2+}]_{in} - [Co^{2+}]_{T}}{[Co^{2+}]_{in}} \quad \text{Eq 2}$$

3. Summary

Homogeneous crystallization in FBR process can be defined as a continuous mass transfer of ions coming from the wastewater streams of CMP (cobalt stream) and etching processes (phosphate stream) to promote cobalt phosphate crystals. Moreover, FBHC becomes attainable at low supersaturation condition in meta-stable region (solubility) (Shih et al., 2016).

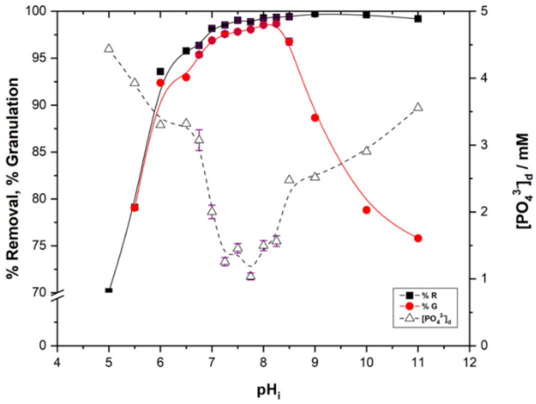

Fig 1. Influence of pH_i in cobalt and phosphate recovery

Influence of pH_i variation from 5.0 – 11.0 from cobalt ion removal which achieved ~99.0% on its optimal conditions is shown in *Fig 1*. Maximum cobalt phosphate granulation of 96.07% were realized at optimum pH_i range of 7.75 – 8.0 and $[PO_4^{3-}]/[Co^{2+}]$ molar ratio 2.0. Phosphate concentration in etching stream was reduced from 14.0 mM to 1.02 mM of $[PO_4^{3-}]_d$ at optimal conditions. Moreover, uniform crystal growth were attained due to appropriate fluidization and proper collision of the particles at hydraulic retention times of 15 min, upflow velocity 34.38 – 40.11 m h^{-1} and surface loadings of 1.18 kg Co^{2+} m^{-2} h^{-1}. The granules recovered were characterized to have selective crystallization of cobalt phosphate octahydrate mineral $Co_3(PO_4)_2.8H_2O$ (PDF No. 00-033-0432) as main products using XRD analysis. In addition, EDS analysis results are ~34.0% Co, ~21.0% P and ~45.0% O. The granules size formed was 0.7 mm in diameters at optimal conditions. SEM analysis showed a petal-like crystal formation of cobalt as shown in *Fig. 2.*
The overall results shows the promising capability of fluidized-bed homogenous crystallization process in recovering heavy metals. The revalorized products can be utilized in several components such as rechargeable batteries, for metal plating , and can be further reused in semiconductor materials making the overall process more sustainable.

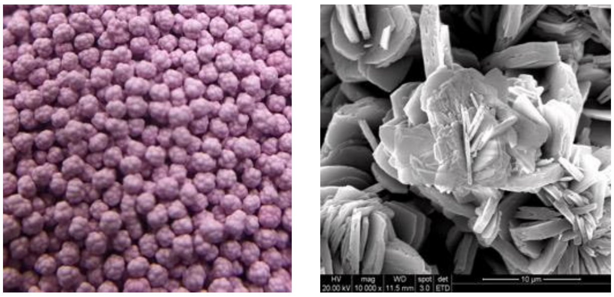

Fig 2. $Co_3(PO_4)_2.8H_2O$ granules at optimum conditions

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