Chemosphere 90 (2013) 674–682

Contents lists available at SciVerse ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Optimisation of the batch reactor for the removal of cobalt ions from chloride media

Soh Wen Min [a], M.A. Hasnat [b], Afidah Abd Rahim [a], Norita Mohamed [a,*]

[a] School of Chemical Sciences, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia
[b] Department of Chemistry, Graduate School of Physical Sciences, Shahajalal University of Science and Technology, Sylhet 3114, Bangladesh

HIGHLIGHTS

- Electrogenerative process as an alternative to electrowinning recovery process.
- Replacement of the conventional sulphate medium.
- Low cost and faster recovery process.
- Cobalt deposition mechanism on RVC electrode.
- Influence of pH on cobalt deposition mechanism.

ARTICLE INFO

Article history:
Received 28 May 2012
Received in revised form 30 August 2012
Accepted 11 September 2012
Available online 12 October 2012

Keywords:
Electrogenerative process
Cobalt recovery
Chloride medium
Free energy
pH
Cell performance

ABSTRACT

A series of experiments were carried out to determine the best medium for the recovery of cobalt by means of an electrogenerative system. Use of the electrogenerative system with a chloride medium had shown promising performance with the highest free energy of -389.8 kJ mol^{-1} compared to that with sulphate and nitrate media. Subsequently, the influence of catholyte concentrations on cobalt recovery using the electrogenerative process was carried out by varying the initial cobalt concentration and sodium chloride concentration. The results showed that almost 100% recovery was attained within 1–4 h of the recovery process. Influence of pH was investigated where the electrogenerative system performed best between pH 5.0 and 7.0. Maximum cell performance of 83% with 99% cobalt removal was obtained at 90 min when 100 mg L^{-1} of Co^{2+} in 0.5 M NaCl was taken as catholyte solution. The values of ΔH^{o} and ΔS^{o} of the process were evaluated as 33.41 kJ mol^{-1} and 0.13 kJ mol^{-1}, respectively.

1. Introduction

Potential applications of cobalt in both scientific and technological fields have made cobalt one of the most sought after heavy metals on earth. The demand for cobalt in recent years has increased significantly due to the rise in manufacturing of electric vehicles and digital components (Bhuiyan et al., 2008). With the public awareness on green technology especially on reducing the usage of natural resources such as petroleum, much research have been focused on producing the next generation of vehicles which rely on electricity to operate. Thus, cobalt has been proven to be most valuable since it is the key element used in designing transformers, motors and generators for electric vehicles. The development of tablet computers and smart phones in recent years also hinge on the increasing usage of cobalt especially in mass production of digital components (Rios-Reyes et al., 2009). Cobalt and cobalt alloys exhibit special properties such as high corrosion resistance, high thermal and electrical conductivities (Chi et al., 2005). These special properties have been utilised in the manufacture of super alloys used in turbine blades for aircraft jet engines and gas turbines for pipelines compressors.

Contrary to its wide array of industrial applications, cobalt is a non-biodegradable heavy metal pollutant. Increasing discharge of cobalt to the environment has led to the accumulation of cobalt in aquatic flora and fauna which then enters the human food chain and harms our ecosystem (Dermentzis et al., 2010). Moreover, improper disposal of cobalt waste through various industrial activities is one of the major causes of water pollution. According to the Canadian Water Quality Guidelines provided by Canada Environmental Bureau of Investigation, the permissible limit of cobalt in irrigation water and livestock waste are 0.05 and 1.0 mg L^{-1}. Health hazards associated with over exposure to cobalt include asthma, dermatitis, gastric disturbance, vasodilatation and cancer. Thus, treatment processes for industrial effluents are essential and have attracted the interests of many researchers.

* Corresponding author. Tel.: +60 4 6534049/6533576; fax: +60 4 6574854.
E-mail address: mnorita@usm.my (N. Mohamed).

0045-6535/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.chemosphere.2012.09.048

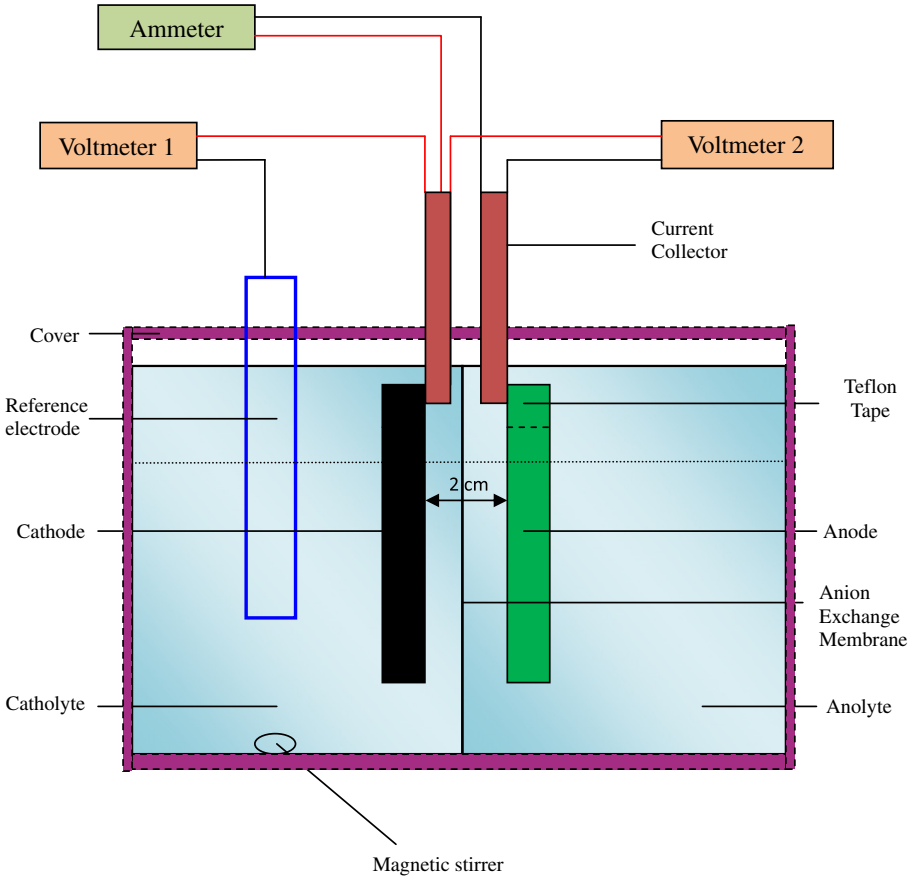

Fig. 1. Experimental setup and electrical circuit.

There are numerous treatment technologies available for the removal of cobalt from industrial effluents. Among them are adsorption on smectite-rich clays (Triantafyllou et al., 1999), solvent extraction (Luo et al., 2006), biosorption using lemon peel (Bhatnagar et al., 2010) and electrodeionization (Dermentzis et al., 2010). However, the focus of this research is on the recovery of cobalt using an electrogenerative system under the influence of chloride medium. This method of treatment offers an efficient and clean way of recycling and recovering both metal and water (Hor and Mohamed, 2003, 2005; Yap and Mohamed, 2007). It is also an attractive alternative treatment process compared to the conventional method of electrowinning because its driving mechanism is a spontaneous electrochemical reaction which does not require an external energy supply.

Electrogenerative recovery of cobalt using a batch cell was first introduced by Tan and Mohamed (2011). This process was carried out in a sulphate medium where recovery of 200 mg L^{-1} cobalt was almost 100% after 10 h of operation. The long period of recovery for cobalt in sulphate medium prompted the possible replacement of the conventional sulphate bath with a chloride bath. According to Kongstein et al. (2007a,b), the chloride medium has better electrical conductivity, lower energy consumption, greater depolarising effect, lower overpotential and higher cathodic current efficiency. Moreover, higher activity coefficients of the cobalt chloride solutions and solubility enable higher concentrations of cobalt to be used in the system (Åkre, 2008).

The merit of using RVC as a cathode in an electrogenerative system has been well established (Hor and Mohamed, 2003, 2005; Tan and Mohamed, 2011; Tan et al., 2012). The purpose of this work is to study the feasibility of the chloride medium in cobalt recovery at RVC cathodes using an electrogenerative process. The performance of the system will be evaluated based on the medium used, initial cobalt(II) concentration, influence of pH and concentration of sodium chloride as a supporting electrolyte. The pH changes during the experiments were monitored to study their effects on cobalt recovery.

2. Experimental

2.1. Voltammetric studies

Cyclic voltammetric experiments were carried out in a 15 mL Pyrex cell with a conventional three electrode system where RVC (RVC 80 ppi, The Electrosynthesis Co.) (0.3 cm × 0.3 cm × 2 cm) served as the working electrode. All the voltammetric experiments were conducted with respect to Ag/AgCl reference electrode, where a platinum wire was used as counter electrode. An eDAQ EA 161 potentiostat connected to a 61 e–corder 410 (4–channel recorder) equipped with EChem software was used to carry out the electrochemical measurements. The salts $CoCl_2{\cdot}6H_2O$, $CoSO_4{\cdot}5H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ were used to prepare 50, 250, and 500 mg L^{-1} of chloride, sulphate, and nitrate solutions of cobalt(II). In order to investigate the effects of different anions, 0.5 M of NaCl, Na_2SO_4 and $NaNO_3$ were added to the chloride, sulphate and nitrate solutions of cobalt(II) respectively as supporting electrolytes. All the electrolytes were prepared from analytical grade reagents (QRëC™) using 18 MΩ cm deionised water. The experiments were carried out at an initial pH 5 at 25 °C. Under these conditions, the predominant cobalt species was the octahedrally coordinated $Co(H_2O)_6^{2+}$ ions giving a red colour to all the electrolytes (Pourbaix, 1966).