Separation and Purification Technology 75 (2010) 303–309

Contents lists available at ScienceDirect

Separation and Purification Technology

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

Feasibility study on the recovery of hexavalent chromium from a simulated electroplating effluent using Alamine 336 and refined palm oil

R.T. Bachmann[a,*], D. Wiemken[a,c], A.B. Tengkiat[b], M. Wilichowski[c]

[a] MICET, Universiti Kuala Lumpur, Lot 1988, Taboh Naning, 78000 Alor Gajah, Malaysia
[b] University of Santo Tomas, España Blvd, Sampaloc, Manila, Philippines
[c] Hochschule Wismar, University of Applied Sciences: Technology, Business and Design, Philipp-Müller-Str. 14, 23952 Wismar, Germany

ARTICLE INFO

Article history:
Received 25 June 2010
Received in revised form 25 August 2010
Accepted 25 August 2010

Keywords:
ALIX
Chromium
Palm oil
Solvent extraction
Electroplating effluent

ABSTRACT

Chromium is an element that is widely used in stainless steel manufacturing, leather tanning and electroplating. Its hexavalent species are toxic and cause of considerable damage if released into the environment. Coupled with depleting reserves and stricter environmental laws it becomes necessary to reduce, reuse and recycle this important commodity.

The objective of the study is to test the suitability of Alamine 336 and a renewable and biodegradable diluent, i.e. refined palm oil, in the recovery of hexavalent chromium from synthetic concentrated electroplating effluents using the anionic liquid ion exchange (ALIX) process. The performance of refined palm oil was compared with kerosene, a flammable nonbiodegradable commercial solvent.

Alamine 336:diluent molar ratios of up to 1:1 can be carried out with refined palm oil over a pH range of 1–4 with a single-step extraction efficiency of up to 95%. Speciation modelling with Visual MINTEQ® suggests a high Alamine 336 affinity for hexavalent chromium species $CrO_3SO_4^{2-}$ and $HCrO_4^-$. The presence of interfering metal ions like iron and zinc slightly suppressed the chromium uptake capability of Alamine 336. Sulphate anions, as well as the presence of copper and nickel ions have no negative effect on Cr(VI) extraction. Visual MINTEQ® has proven to be a useful tool in solving relatively complex metal speciation and solubility problems encountered in ALIX extraction.

The findings of this study provide a significant step towards a greener and safer chromium recovery process in the electroplating industry but also commercial and academic analytical laboratories.

1. Introduction

Rapid industrialisation and growth in population over the past 200 years exert an increasing pressure on natural resources and the environment. Billions of tons of controlled and scheduled waste are generated every year by the industrial sector worldwide which is often either pretreated on-site or at a licensed contractor prior to final disposal in landfills. This practice if continued is leading to resource depletion and creates a potentially harmful legacy for future generations. In order to move towards a more sustainable development as outlined in the Bruntl and Report (1987), waste reduction, reuse and recycling coupled with pollution prevention and/or pollution control measures play an important role to slow down if not reverse this practice.

Heavy metals such as cadmium, mercury, lead and chromium are not degradable or renewable like biomass hence if they are to be used in future processes, reuse and recycling are the only options. At present, heavy metals are used in the chemical industry sector for applications ranging from batteries to catalysts and surface coatings, and can be found at various concentrations in gaseous, liquid or solid waste.

Chromium, for example, is used in the ferrochromium (85%), chemical (8%) and refractory industry (7%) [1,2]. Chromium is primarily obtained from chromite ore. South Africa, Kazakhstan and Zimbabwe are the main chromite exporters possessing 6.5 billion tons or 97% of the proven chromite reserves worldwide [3–6].

The annual worldwide production of chromium increased exponentially since recorded history started about a hundred years ago (Fig. 1). Papp [6] estimated that 26% of the chromium produced worldwide in 1993 has dissipated to the environment. Chromium is also of particular interest owing to its legislative status and unique chemistry. Chromium exists in nature primarily in one of two oxidation states [7,8]. There are other chemical oxidation states of chromium, which include 0, II, IV, and V, but they are considered transitory compared to more stable trivalent Cr(III) and hexavalent Cr(VI) species. Hexavalent chromium is a strong oxidizer which can react with DNA causing mutation. On the other hand, the organically complexed trivalent form is used as a dietary supplement that

---

* Corresponding author. Tel.: +60 6 551 2086; fax: +60 6 551 2001.
E-mail address: bachmann@micet.unikl.edu.my (R.T. Bachmann).

1383-5866/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.seppur.2010.08.019

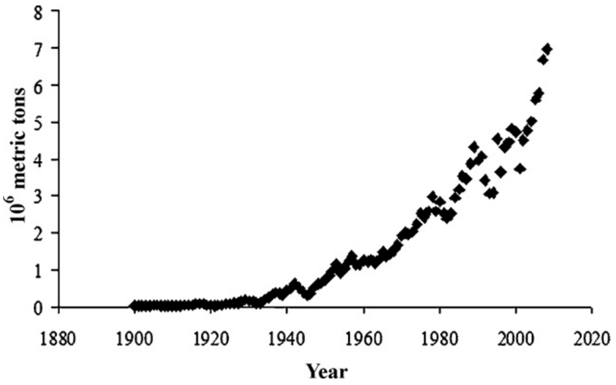

Fig. 1. Annual worldwide chromite ore production since 1900 [1].

helps in glucose metabolism, weight loss and muscle toning [7]. Unlike many other metals, Cr(VI) can combine with oxygen to form water-soluble, negatively charged anions known as yellow chromate (CrO_4^{2-}) or orange dichromate ($Cr_2O_7^{2-}$), which adsorb to positively charged sites in contrast to cationic metal species [7]. Therefore, hexavalent chromium species are not strongly sorbed in many soils under alkaline to slightly acidic conditions. Thus, they can be very mobile in subsurface environment, while other metals precipitated out, and exert toxic effects on biological systems.

Various well-established methods may be used to treat industrial effluents and contaminated water such as reduction and precipitation [9,10], reverse osmosis [11], evaporation [11], ion exchange [12] and adsorption [13,14]. While these processes are able to remove the pollutants from the waste stream to meet stringent discharge limits, they may produce concentrated waste and be less suitable for efficient and selective material recovery. Solvent extraction, on the other hand, is one of the most effective conventional methods extensively used in separation technology [15], with potential to selectively recover metals from industrial effluents that can also be operated in a closed loop. Various reviews dealing with solvent extraction of chromium and other heavy metals are available [15–17]. Several ion-association forming systems such as triisooctylamine (TIOA) [18], tetrabutylammonium bromide (Aliquat 100) [19,20], trioctylmethylammonium chloride (Aliquat 336) [21–26], trioctylamine (Alamine 336) [27], triphenylsulphonium (TPS) [28] and triphenylphosphonium (TPP) [28,29] had been studied to extract chromium in the anionic form (Fig. 2).

In this study Alamine 336, a tertiary amine, will be used for hexavalent chromium extraction. According to supplier information [30], the Alamine series of reagents exhibit the following general extraction chemistry:

$$[R_3N]_{org} + [HA]_{aq} \Leftrightarrow [R_3NH^+A^-]_{org} \tag{1}$$

$$[R_3NH^+A^-]_{org} + [B^-] \Leftrightarrow [R_3NH^+B^-]_{org} + [A^-] \tag{2}$$

Eq. (1) illustrates amine salt formation with R representing a variety of hydrocarbon chains, and Eq. (2) represents true ion exchange. The extent to which B^- will be exchanged for A^- is a function of the relative affinity of the two anions for the organic cation and the relative stability of the anions in the aqueous medium. Typically, extraction favours larger low-charged anions over smaller highly charged anions.

A number of extractants have been used for the recovery of Cr(VI) such as:

- Aqueous solution of $(NH_4)_2SO_4$ [19],
- Hydrocarbons like methyl isobutylketone [20,31], benzene [32], hexane [32,33], toluene [33], xylene [32] and kerosene [25,26,32–35],
- Halogenated organics like chloroform [18,21,32,33], dichloroethane [29], and dichloromethane [20],
- Tri-n-butylphosphate [36].

Most of these solvents are acceptable for use in lab-scale extraction processes but are unsuitable for industrial-scale extraction processes due to economical, health, safety and environmental concerns. Of all the solvents cited above, kerosene appears to be the preferred industrial solvent of choice.

Kerosene, a mixture of various hydrocarbons obtained by distillation of petroleum at boiling point range 175–330 °C [37,38], is mainly used as an aircraft gas turbine and jet fuel by both commer-

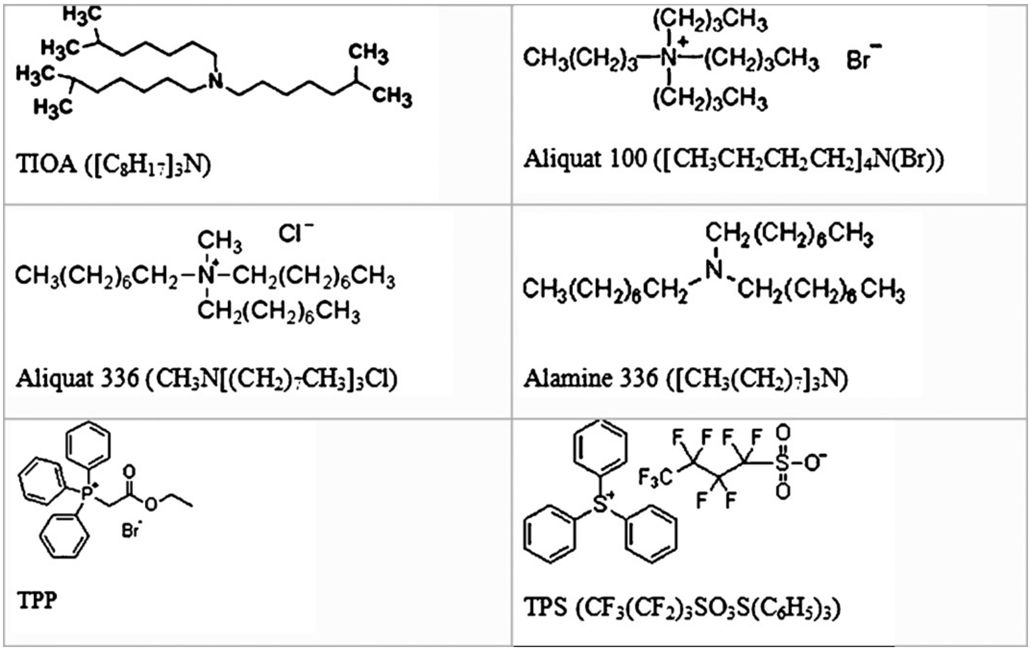

Fig. 2. Chemical structure and formula of various extractants used in chromium recovery processes.