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ORIGINAL ARTICLE

Hexavalent chromium recovery by liquid–liquid extraction with 2-octylaminopyridine from acidic chloride media and its sequential separation from other heavy toxic metal ions

C.P. Mane [a], S.V. Mahamuni [b], S.S. Kolekar [d], S.H. Han [c], M.A. Anuse [d,*]

[a] *Department of Chemistry, Lal Bahadur Shastri Mahavidyalaya, Satara, India*
[b] *Department of Chemistry, Sadguru Gadage Maharaj College, Karad, India*
[c] *Inorganic Nano-Materials Laboratory, Department of Chemistry, Hanyang University, Seoul 133-791, Republic of Korea*
[d] *Analytical Chemistry Laboratory, Department of Chemistry, Shivaji University, Kolhapur 416 004, India*

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Abstract A systematic study of extraction of chromium(VI) with 2-octylaminopyridine (2-OAP) in xylene at room temperature has been conducted. Quantitative extraction of chromium(VI) was observed in the 0.4–0.8 M concentration range of hydrochloric acid. From the extracted complex species in the organic phase, chromium(VI) was back extracted with 7 N ammonia (3 × 10 mL), and was determined by spectrophotometric method. Various parameters such as 2-OAP concentration, equilibrium period, effect of various diluents, aqueous: organic volume ratio, acidity and diverse ions were studied. The extraction reaction proceeds with ion-pair formation and the stoichiometry of extracted species was found to be $[(2OAPH^+)\ CrO_3Cl^-]_{(org)}$. The separation and determination of chromium(VI) from associated and toxic metals in binary, ternary and multicomponent mixture were carried out. The method permits the sequential separation of chromium(VI) from other toxic metals and

* Corresponding author. Tel.: +91 231 2609380; fax: +91 231 2692333.
E-mail address: mansinganuse@yahoo.co.in (M.A. Anuse).

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has been used to separate and determine chromium(VI) from alloys, and effluent water samples from tannery industries.

1. Introduction

Chromium is used for the production of stainless steel, chrome plated metals, pigments and chemicals. The main chromium emissions into surface water are from metal-finishing processes such as electroplating pickling and bright dipping. Uncontrolled emissions are potential contaminating sources in fresh waters, especially with regard to the toxic chromium(VI). Other discharges of chromium(VI) are related to the additives in circulating cooling waters, laundry chemicals and animal glue manufacture (Pannain and Santelli, 1995). Owing to the high oxidation potential and the ease of penetration from biological membranes, chromium(VI) compounds are approximately 100 times more toxic than chromium(III) salts. Moreover, in environment air, chromium particulates play a role in the oxidation of sulphur dioxide and the formation of acidic aerosols involved in global acid rain (Bag et al., 2000).

Toxicity of chromium compounds depends on its oxidation state (Goldoni et al., 2006). Chromium(VI) compounds were found to be toxic for living organisms. Human toxicity includes lung cancer as well as kidney, liver and gastric damage, hence chromium(VI) is one of the major toxic element present in environmental samples (Kozlowski et al., 2002). In view of these facts, the separation and determination of chromium at trace levels have received considerable attention for the ease of manipulation and routine operation.

High molecular weight amines (HMWA's), termed as 'liquid anion exchangers', are used in liquid–liquid extraction for many metals as they have low water solubility and high miscibility in organic solvents. The quaternary ammonium salts such as trioctylmethylammonium compounds (aliquat 336) (Lo and Shiue, 1998), alamine 336 and aliquat 336 (Vincent and Guibal, 2000) and alamine 336 (Senol, 2004) played important role in liquid–liquid extraction of chromium(VI). Chromium(VI) has been extracted with liquid anion exchanger, amberlite LA 1 and LA 2 in methyl isobutyl ketone (MIBK) from waste water and sludge (Stasinakis et al., 2003), urine (Claudio et al., 1983) and aerosol particles (Nusko and Heumann, 1997). Liquid–liquid extraction of chromium(VI) from sulphuric acid solution with tri-*n*-dodecylamine (Jamal, 2007) containing octanol-1 as a modifier in kerosene was investigated. Separation and recovery of chromium(VI) from simulated plating waste aqueous solution using microcapsules consisting of styrenedivinylbenzene copolymer and containing tri-*n*-octylmethylammonium chloride (TOMAC) or bis (2-ethylhexyl) phosphoric acid (D2EHPA) as the extractant were studied (Nishihama et al., 2004).

The chromium(VI) was complexed by the reaction with ammonium pyrolidine dithiocarbamate (APDC). The chromium(VI) complex in organic extract was determined by HPLC (Wang and Chiu, 2004) and inductively coupled plasma mass spectrometry (Li et al., 2002). The determination of hexavelant chromium in fresh and saline waters is based on the reaction of chromium(VI) with diphenyl carbazide (DPC) (Gardner and Comber, 2002). An on-line dynamic two dimensional admicelles solvent extraction system was coupled to electrothermal atomic absorption spectrometry (ETAAS) for determination of chromium(VI) with pyrolidine dithiocarbamate (Nan and Yan, 2005) in drinking water. The content of chromium(VI) in water was determined by air-acetylene FAAS after being enriched by ammoniumpyrolidinedithiocarbamate-diethyldithiocarbamate-methyl *iso*butyl ketone APDC (Xiuxiang et al., 1999)/DDTC (Xiuxiang et al., 1999; Tang et al., 2004)/MIBK (Tang et al., 2004) system in which APDC and Na-DDTC were complexing agents and MIBK was extracting agent. Diperoxochromium creates a complex with ethyl acetate (Beni et al., 2007) while, chromium(III) remains in the aqueous phase. The chromium(VI) content of ethyl acetate phase was determined with graphite furnace atomic absorption spectrometry. The reported method was applied for the separation of chromium(VI) from chromium(III).

A supported liquid membrane (SLM) technique was investigated for extraction and pre-concentration of chromium(VI) by using aliquat 366 (Lorraine et al., 2002).

The economic recovery and concentration of chromium(VI) from waste water was investigated using an emulsion liquid membrane (ELM) containing aliquat 336 chloride (Datta and Agrwal, 1999; Bhowal and Datta, 2001; Chakraborty et al., 2005a,b; Banerjea et al., 2000) as an extractant and SPAN 80 as surfactant. An attempt has been made to extract chromium(VI) through emulsion liquid surfactant membrane or emulsion liquid membrane (ELM) from its acidic solution, using alamine336 (Chakraborty et al., 2005a,b) and caustic soda as an extractant and stripping reagent, respectively. Around 97% extraction of chromium(VI) from aqueous solutions of potassium dichromate through batch experimentation has been achieved.

Extraction of chromium(VI) from sulphuric acid aqueous solution using a liquid surfactant membrane (LSM) containing tributyl phosphate (TBP) (Chiha et al., 2006; Vohra et al., 1989) was studied. The influence of the sodium hydroxide concentration on stripping efficiency was investigated. The extraction of chromium(VI) through a liquid surfactant membrane, tributyl phosphate (TBP) and trioctylphosphinoxide (TOPO) (Frites et al., 2005) dissolved in dodecane considered as a carrier was reported. Triethanolamine was used as an inner phase reagent. The solvent extraction of chromium(VI) in chloroform, dichloromethane, dichloroethane and its transport through a chloroformic bulk liquid membrane from sulphuric acid solutions with neutral extractant triphenyl phosphine (TPP) (Sachmoune and Mitiche, 2004) was studied. The co-extraction and the co-transport of sulphuric acid is very low and has no effect on the transport efficiency. The extraction of hexavelant chromium from aqueous solution by cocob betaine (Singh et al., 2002) in a mixture of kerosene and benzene was investigated. In acidic solution the extraction efficiency of chromium(VI) was excellent. However, the relative affinities of NO_3^-, Cl^- and SO_4^{2-} to cocob betaine were also considerable. Synthesis of calix [4] arene diamide derivatives (Bozkurt et al., 2005) was reported and used for the extraction of chromium(VI). The complexation ability of calix [4] arene was studied and it was based on the receptors.

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