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Combined cation-exchange and extraction chromatographic method of pre-concentration and concomitant separation of Cu(II) with high molecular mass liquid cation exchanger after its online detection

B. Mandal*, U.S. Roy, D. Datta, N. Ghosh

Department of Chemistry, Visva-Bharati University, Santiniketan 731235, India

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ABSTRACT

A selective method has been developed for the extraction chromatographic trace level separation of Cu(II) with Versatic 10 (liquid cation exchanger) coated on silanised silica gel (SSG-V10). Cu(II) has been extracted from 0.1 M acetate buffer at the range of pH 4.0–5.5. The effects of foreign ions, pH, flow-rate, stripping agents on extraction and elution have been investigated. Exchange capacity of the prepared exchanger at different temperatures with respect to Cu(II) has been determined. The extraction equilibrium constant (K_{ex}) and different standard thermodynamic parameters have also been calculated by temperature variation method. Positive value of ΔH (7.98 kJ mol^{-1}) and ΔS (0.1916 kJ mol^{-1}) and negative value of ΔG (-49.16 kJ mol^{-1}) indicated that the process was endothermic, entropy gaining and spontaneous. Preconcentration factor was optimized at 74.7 ± 0.2 and the desorption constants $K_{desorption}{}^1(1.4 \times 10^{-2})$ and $K_{desorption}{}^2(9.8 \times 10^{-2})$ were determined. The effect of pH on R_f values in ion exchange paper chromatography has been investigated. In order to investigate the sorption isotherm, two equilibrium models, the Freundlich and Langmuir isotherms, were analyzed. Cu(II) has been separated from synthetic binary and multi-component mixtures containing various metal ions associated with it in ores and alloy samples. The method effectively permits sequential separation of Cu(II) from synthetic quaternary mixture containing its congeners Bi(III), Sn(II), Hg(II) and Cu(II), Cd(II), Pb(II) of same analytical group. The method was found effective for the selective detection, removal and recovery of Cu(II) from industrial waste and standard alloy samples following its preconcentration on the column. A plausible mechanism for the extraction of Cu(II) has been suggested.

1. Introduction

Copper is a harmful toxic element and has got technical importance because of its high thermal and electrical conductance. In trace level heavy metals like Cr(III), Cd(II), Zn(II), Hg(II), Pb(II) and Cu(II) etc., are hazardous to the environment [1]. The removal of heavy metal ions from industrial waste waters is becoming more relevant with the increase of industrialization [2]. Trace level monitoring of metallic toxicant poses a challenging problem to the analytical chemists. However, preconcentration and separation of an analyte is usually necessary before its monitoring. In this regard, the most widely used techniques are solvent extraction [3], coprecipitation [4–6], ion chromatography [7], adsorption [8,9], cloud point extraction [10], electrochemical deposition [11] and solid phase extraction (SPE) [12–14]. But, except SPE all other techniques are extremely expensive, when the metals are in large volumes of relatively low concentrations [15]. SPE [16–18] is an analytical technique for the trace level separation and preconcentration of heavy metals. It is simple, selective, rapid, ecofriendly, cost effective and has high enrichment factor. In our laboratory, Versatic 10 on hydrophobic silica support has been used for the extraction, separation and preconcentration of Bi(III) [19]. But the systematic extraction chromatographic investigation of Cu(II) with HMMCA, Versatic 10 on silanised silica gel for simultaneous detection and separation at trace level after its preconcentration at the column has yet not been reported. Versatic 10, is a mixture of C_{10} isomeric tertiary monocarboxylic acids, had the concentration and purity of 5.2 M and 99% (w/v) respectively [20]. It is soluble in several solvents like benzene, toluene, *n*-hexane, xylene, butanol, carbon tetrachloride, chloroform, nitrobenzene and diisopropyl ether [21,22]. It has a good thermal and chemical stability [20] and efficiently extracts metal ions from aqueous solution over a wide range of pH [23,24]. The present work reports a rapid method for the extraction, preconcentration, detection and separation of microgram level Cu(II) from wide variety of multi-component mixtures

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* Corresponding author. Tel.: +91 9474738517; fax: +91 3463261526.
E-mail address: bhabatosh_mandal@yahoo.co.in (B. Mandal).

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containing large number of heavy, toxic and conger cations with HMMCA, Versatic 10 on hydrophobic silica support.

2. Experimental

2.1. Apparatus

Digital Elico L1-120 pH meter combined with glass electrode, 7D-1F thermostat, spectrophotometer (Beckman DU-6 ECIL GS 5700A), Shimadzu FTIR spectrophotometer (model no FTIR-8400S), Simadzu atomic absorption spectrophotometer (model no. 6300), Thermo Scientific (Orion 5 Star Benchtop Multi W/ISE mtr, Singapore) and chromatographic glass column (0.8 cm × 8 cm) were used in the present study.

2.2. Reagents

Unless otherwise stated, all chemicals and solvents used in this work were of analytical grade (BDH/E Merck). A liquid cation exchanger, Versatic 10 (Shell Chemical, London, England), a mixture of highly branched aliphatic C_{10} isomeric tertiaty monocarboxylic acid, was used without any further purification. Dimethyldichlorosilane (BDH, Mumbai, India) was used for end capping of silica gel (BDH, Mumbai, India) (120 mesh). A standard stock solution of Cu(II) (1.06 mg cm^{-3}) was prepared by dissolving $Cu(NO_3)_2$ (E. Merc, Mumbai, India) in water and estimated complexometrically [25] with EDTA (E. Merc, Mumbai, India) using xylenol orange (BDH, Mumbai, India) as indicator. The solution containing 10.6 μg cm^{-3} of Cu(II) was prepared through appropriate dilution. This concentration (10.6 μg cm^{-3}) of Cu(II) has been selected randomly for our present work. Buffer solutions of different pHs were prepared using acetic acid (BDH, Mumbai, India) (0.1 M) and ammonium acetate (BDH, Mumbai, India) (0.1 M) in proper ratio. Lower pH values were adjusted with the help of 0.2 M chloro-acetic acid.

2.3. Preparation of ion exchange material

Silica gel (60–120 mesh) was made hydrophobic by exposing it to the vapor of dimethyldichlorosilane (DMDCS) in N_2 atmosphere. The DMDCS treated (silanised) silica gel was then washed with anhydrous methanol and dried at 70–80 °C. The silanised silica gel (SSG) was impregnated with Versatic 10 (V 10), diluted in diisopropyl ether (0.2 mL in 100 mL) and was dried in a rotary vacuum evaporator to achieve uniform coating [19]. The surface area of exchanger was determined by standard methylene blue method [26]. The exchanger (SSG-V10) could be used for at least 40 cycles without any loss of its exchange capacity. For ion-exchange paper chromatography, a strip of Whatman No 1 was immersed in a solution of Versatic 10 (0.2 mL was taken in 20 mL diisopropyl ether) to achieve uniform coating and then dried in air. Cu(II) in μg level was spotted on the paper strip containing exchanger and developed with acetate buffer of pH 5.0:acetone (15:2, v/v).

2.4. General extraction procedure

An aliquot of Cu(II) solution (10.6 μg mL^{-1}) in acetate buffer of pH 5.0 was passed through the column (pre-adjusted pH 5.0) containing ion exchanger (1 g), at a flow rate of 1.0 cm^3 min^{-1}. After extraction, Cu(II) was stripped with 0.1 M HNO_3 and the amount of Cu(II) was determined by ion selective electrode.

2.5. Batch procedure

2.5.1. Distribution co-efficient (K_d)

A total 100 mg of the dry exchanger was suspended with constant stirring in 400 cm^3 Cu(II) solution (10.6 μg cm^{-3}) for 30 min at the desired pH value in the range 2.5–7.5. The same experiment has also been made in presence of acetate ion in the range 50–300 ppm at pH 5.0. The supernatant was filtered through a dry filter paper immediately. The amount of Cu(II) in the filtrate was determined by Ion selective electrode.

2.5.2. Adsorption isotherm

A total 100 mg of the dry exchanger was suspended with constant stirring for 30 min in 400 cm^3 of Cu(II) solution with different initial concentrations (10–80 μg cm^{-3}) at pH 5.0. The amount of Cu(II) adsorbed per unit mass of the adsorbent (q_e in mg g^{-1}) was computed using the following equation:

$$q_e = (C_i - C_e) \times \frac{V}{m} \quad (1)$$

Here, C_i and C_e are the initial and equilibrium concentrations (mg dm^{-3}), m is the mass (g) of the adsorbent, and V (dm^3) is the volume of the solution.

3. Results and discussion

3.1. FTIR analysis

The decreasing of stretching frequency (1703 to 1660–1540 cm^{-1}) in the loaded exchanger indicates the conversion of –COOH group to $–COO^-$ ion [27] and suggests the participation of this functional group in the adsorption of Cu(II) by the exchanger.

3.2. Exchange capacity of the prepared exchanger

The exchange capacity of the prepared exchanger was determined [22] at different temperatures by measuring the milliequivalent of sodium ions adsorbed by 1 g of dry exchanger in H^+ form. The exchange capacity at pH 10–12 and temperature 27–40 °C was found to be 2.56 mequiv. of H^+ g^{-1} of dry exchanger and it is consistent with the literature value [19,28]. It corresponds to the maximum uptake capacity of the exchanger for Cu(II) and it was 1.28 mequiv (81.28 mg g^{-1}) at the said pH.

3.3. Break through capacity (maximum uptake capacity) and preconcentration factor

The pHs of the exchanger bed and Cu(II) solution (0.053 mg cm^{-3}) were adjusted to the desired value with 0.1 M acetate buffer and then Cu(II) solution in buffer was passed through the column containing 1 g of dry exchanger at a flow-rate of 1.0 cm^3 min^{-1}. The column was saturated with Cu(II) at pHs 4.5, 5.0 and 5.5 on passing 634 cm^3 (33.6 mg), 675 cm^3 (35.8 mg) and 738 cm^3 (39.1 mg) of metal ion solution, respectively. So the maximum uptake capacity of Cu(II) in the column increases with the increase in pH. Here, the working pH (4.5–5.5) is much lower than the required pH (10–12) for full functioning of the exchange site and so the efficiency of the exchanger stands at somewhat reduced level of 41.3–48.1% with respect to Cu(II). After saturation through extraction, Cu(II) was eluted from column with 10 cm^3 0.1 M HNO_3. During this continuous extraction, Cu(II) has been accumulated gradually on the column from its influent of lower concentration (0.053 mg cm^{-3}) and after elution the effluent (10 cm^3) were found to be enriched with higher concentrations (3.34 mg cm^{-3}, 3.56 mg cm^{-3}, 3.87 mg cm^{-3}) (99% recovery) of