EXTRACTION OF Co(II) AND Cu(II) FROM WASTE MATERIALS WITH SEMICARBAZONE OF 4-NITROBENZALDEHYDE

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ABSTRACT

The studies on extraction of Co(II) and Cu(II) from aqueous solutions of waste material into the organic phase using 4-nitrobenzaldehydesemicarbazone were found to be sufficient. However, it was observed that the extraction increases when the pH of the solution was increased and extraction was found to be higher for Cu(II) in comparison with Co(II). This supports the following type of extraction mechanism.

$(M^{n+})_{aq} + m (HL)_{org} = [ML_n (m-n)HL]_{org} + n(H^+)_{aq}$

The extraction decreases with increased concentration of metal ion whereas the Sandell sensitivity and metal/ligand ratio were found to be $0.0049 \mu\text{gcm}^{-2}$ and 1:2 respectively. The determination of Co(II) and Cu(II) has also been executed in the existence of foreign ions.

Keywords: Solvent Extraction, 4-Nitrobenzaldehydesemicarbozone, Semicarbazone, Thiosemicarbazones.

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INTRODUCTION

The waste material at the industrial site has evolved as a major problem, for which the solvent extraction method would be preferably best for the extraction of precious metal from them. Semi and thiosemicarbazones are a class of compounds possessing a wide spectrum of medicinal properties.^{1,36} The carcinostatic properties of metal complexes of thiosemicarbazide and thiosemicarbazones have captivated great attention.² The 1-methyl isatin thiosemicarbazone (Marboran) is a specific preventive drug of smallpox.³ For detecting zinc by luminescence method the salicylaldehyde semicarbazone has also been used.⁴

Phenanthrenequinone monosemicarbazone (PQSC) was used as an extractive indicator in the complexometric determination of cobalt with EDTA by using 8-10 drops of a 0.3% solution of the indicator in CHCl_3 , the titration can be successfully carried out at room temperature over the pH range⁵ 8.3- 10.0.

The phenanthrene Quinone monothiosemicarbazone reagent was also used⁶ for the precise and efficient determination of Fe(II) and Fe(III).

The preparation, stability and ionization constants of 2-hydroxy-3-methyl-2-cyclopentane-1-onethiosemicarbazone (I) and 3-methyl-1,2-cyclopentanedione bithiosemicarbazone(II) were reported⁷. For trace determination of Zn(II) and Bi(II) one of the significant compound Ni(II)-EDTA-6-methylepicolinealdehyde azine was used.⁸

The fluorometric properties of the oxime thiosemicarbazone, azine and 2-pyridylhydrazone derivatives of 3-hydroxy-2-pyridine carbaldehyde⁹; spectrophotometric determination of vanadium with salicylaldehyde thiosemicarbazone¹⁰; dibenzoyl methane thiosemicarbazone as an analytical reagent for determination of Pt(IV), Co(II), Mo(II), Pd(II), Ni(II), and Cu(II)¹¹⁻¹² has also been studied.

Some more documented literature involve studies such as the development of 1,3-cyclohexanedione bithiosemicarbazone monohydrochloride (1,3-CHTD.HCl) for spectrophotometric determination of Nickel (II); spectrophotometric determination of chromium(VI) using cyclohexane-1,3-dione bithiosemicarbazone monohydrochloride¹⁴; determination of Fe(III) and Mn(II) based on the

oxidation of 2-hydroxybenzaldehyde thiosemicarbazone by H_2O_2 in an ammonical medium¹⁵. One another method¹⁶ has reported the spectrophotometer determination of iron (III) and Cu (II). The determination of 1,2-diamino cyclohexane tetraacetic acid involves dissolution in EtOH, the addition of 2-hydroxy benzaldehyde thiosemicarbazone, H_2O_2 , NH_3 and then Mn^{+2} as a catalyst and measuring the fluorescence excitation at 365 nm, emission at 440nm¹⁷. A spectrophotometric method¹⁸ was used to determine the protonation constants of the biacetyl(2-pyridyl)hydrazone-thiosemicarbazone. A new synthesized reagent 5,5-dimethyl- 1,2,3-cyclohexane trione- 1,2- dioxime-3- thiosemicarbazone was spectrophotometrically studies for determination of Fe¹⁹. Recently, Extracted Co(II) with 2,4-dihydroxy acetophenone thiosemicarbazone from NH_4Cl - NH_4OH buffer solution at pH6.5 in BuOH. Co(II) forms a 1:1 complex with thiosemicarbazone.²⁰ An extraction photometric determination method²¹ for Cu and Fe is based on the extraction of their complexes with quinalene-2-aldehydethiosemicarbazone at pH 7.5 into CHCl_3 .

A new extractive spectrophotometric method²² for the determination of Mo is based on the extraction of the orange-red Mothio-cyanato-2-acetylpyridinethiosemicarbazone complex into CHCl_3 from HCl. Manganese is a conventional trace element for human beings.³⁷ Some of the recent reports include the Mn^{II} catalyzed periodate oxidation of aromatic amine.²³⁻²⁶ It is worth mentioning that some methods²⁷⁻²⁸ have been developed for the determination of anilines by employing the reactions of periodate in presence of Mn^{II} . There are a few reports accessible within the literature concerning the kinetic spectrophotometric estimation of Mn^{II} , based on the reduction of periodate ion by some substrates.²⁹⁻³³ The reports are available on stability constant for the ternary intermediate complex formation between aromatic amine, Mn^{II} and periodate³⁴. Most of the precious metal is very essential for human beings, so these are extracted from waste material. This paper describes the extraction of metal ions Co(II) and Cu(II) from the waste material of aqueous solutions into the organic phase using 4-nitrobenzaldehydesemicarbazone.

EXPERIMENTAL

Materials and Methods

All the chemicals were of AR grade. Copper acetate (E. Merk), Cobalt Chloride (E. Merk), Semicarbazidehydrochloride (E. Merk), 4-nitrobenzaldehyde(E. Merk), Acetone(CDH), Chloroform(CDH), Hydrochloric acid(CDH), Disodium hydrogen phosphate(E. Merk), Citric acid(E. Merk), Borax(CDH) Sodium acetate(E. Merk), Acetic acid(E. Merk), Potassium dihydrogen phosphate(E. Merk) and solutions were prepared by using triply distilled water. 4-nitrobenzaldehydesemicarbazone was prepared by the reported method³⁵. The concentration of metal ions in the aqueous phase was determined by using the atomic absorption spectrophotometer (Perkin -Elmer atomic absorption spectrophotometer model 3100). The pH measurements of the aqueous phase before and after equilibration were carried on a combined electrode pH meter (Toshiniwal).

Synthesis of 4-Nitrobenzaldehydesemicarbazone

Semicarbazide hydrochloride (1.12g, 0.01 mole) in 20 ml of methanol was added to the solution and 4-nitrobenzaldehyde (1.50g, 0.01 mole) in methanol (20 ml). The mixture was refluxed for 4 hr with constant stirring. The excess of the solvent was removed by the distillation and creamish color solid was separated by cooling. It was recrystallized from methanol with 85% yield, M.P.-201 °C. The nitrogen in the semicarbazone was determined by Kjeldahl method³⁶. The observed % of N was 26.79 and the calculated % of N was 26.92. It is soluble in chloroform, methanol, ethanol and DMF. The ligand was used as extractants for the solvent extraction of Co(II) and Cu(II) at different pH.

Notably, HNO_3 , H_2SO_4 , and HCl-based solutions were commonly employed for dissolving precious metal from waste materials. The solution of metal ions was prepared by dissolving waste material in H_2SO_4 or HCl. Further, the metal ions solutions were diluted by distilled water. The concentration of the copper and cobalt in the diluted sample was determined on a Perkin- Elmer atomic absorption spectrophotometer. First of all, a standard solution (10^{-2}M) of Cu(II) was prepared and then diluted to prepare four solutions containing 1.0ppm, 2.0ppm, 3.0ppm, and 4.0ppm Cu(II) ions. These solutions were used to calibrate the apparatus used for outlining the plot between absorbance and concentration of the metal ion concluding the concentration of that particular metal ion in the sample solution.

Similarly, the standard solution of 10^{-2} M of Co(II) prepared in distilled water then diluted to prepare five solutions containing 2.0ppm, 4.0ppm, 5.0ppm, and 7.0ppm of Co(II) ions. These solutions were used to calibrate the instrument. The concentration of Co(II) in the solutions before and after extraction was determined directly on the spectrophotometer.

Extraction Procedure

Equal volumes (20.0ml) of aqueous phase consisting of the metal ion in the buffer solution of the desired pH and organic phase (CHCl_3) containing the extractants were shaken at room temperature ($35.0\text{ }^\circ\text{C} \pm 3.0^\circ\text{C}$) for 15 minutes to ensure complete equilibration. The clear phase separation was determined by atomic absorption spectrophotometer. The same procedure was adopted for 2nd extraction of the aqueous phase. The calculations of the concentration of metal ions in the organic phase were determined by noting the difference of original metal ion concentration in the aqueous phase before and after equilibration. The distribution ratio (D) was calculated by the ratio of the concentration of metal ions in the organic phase and concentration of metal ions in the aqueous phase, the percentage extraction (% E) was calculated by (concentration of a metal ion in organic phase / total concentration of metal ion) $\times 100$.

RESULTS AND DISCUSSION

The extraction of metal ions Co(II) and Cu(II) from aqueous solutions into the organic phase using 4-nitrobenzaldehydesemicarbazone was found to be sufficient. However, it was observed that the extraction increases when the pH of the solution was increased and extraction was found to be higher for Cu(II) as compared to Co (II).

Speciation of pH

The present extraction of Co (II) and Cu (II) with 4- nitrobenzaldehydesemicarbazone in chloroform as a function of pH was studied using the buffer of three different pH. The buffer used as follows:

pH = 2.60; Na_2HPO_4 + Citric acid

pH = 4.40; CH_3COONa + acetic acid

pH = 6.89; Na_2HPO_4 + KH_2PO_4

The results of the extraction are given in Tables-1 and 2.

Fig.-1: Effect of pH on Extraction of Cu^{II} with 4-Nitrobenzaldehyde Semicarbazone at $[\text{NBS}] = 2 \times 10^{-2}$ M, $[\text{Cu}(\text{II})] = 1 \times 10^{-2}$ M

Table-2: Extraction of Copper with 4-Nitrobenzaldehyde Semicarbazone as a Function of pH
[NBS] = 2×10^{-2} M, [Cu (II)] = 1×10^{-2} M

pH	% Extraction	D	-LogD
2.60	21.01	0.2660	0.7276
4.40	30.72	0.3110	0.5072
6.89	47.10	0.8902	0.0506

Table-3: Extraction of Co with 4-Nitrobenzaldehydesemicarbazone as a Function of pH
[NBS] = 2×10^{-2} M, [Co (II)] = 1×10^{-2} M

pH	% of Extraction	D	-Log D
2.60	18.75	0.2307	0.6369
4.40	20.01	0.6425	0.6081
6.89	39.05	0.6425	0.1921

Fig.-2: Effect of pH on Extraction of Co^{II} with 4-Nitrobenzaldehyde Semicarbazone at
[NBS] = 2×10^{-2} M, [Co (II)] = 1×10^{-2} M

It was found that % increase with an increase in pH of the aqueous phase. This supports the following type of extraction mechanism-

Further studies were carried out at pH= 6.89 for both Cu (II) and Co (II). The plot of log D versus pH at constant metal ion [Co(II) and Cu(II)] and semicarbazone concentration gave a straight line(Fig.-1 and 2) with a slope of nearly $\sim 1.0 - 1.6$ indicating the possibility of coordination of the semicarbazone to the metal ions in the neutral ketonic form.

Speciation of Metal ion Concentration

The effect of Cu(II) and Co(II) ion concentration within the range ($1.0-5.0 \times 10^{-3}$) on the distribution ratio was studied at constant ligand concentration (10^{-2} M) and constant pH 6.89 as shown in Fig.-3. The results are given in Tables-3 and 4. It was observed that the extraction was almost independent of the metal ions concentration in the above range and there was only a slight decrease in the percent extraction with an increase in metal ions concentration. This rules out the possibility of extraction of any polymeric species in the above-mentioned concentration range.

Fig.-3: Effect of Metal Ion Concentration of the Extraction of Co^{II} and Cu^{II} with 4-Nitrobenzaldehyde Semicarbazone at [NBS] = 1×10⁻² M, pH = 6.89

Table-3: Extraction of Cu(II) with 4-Nitrobenzaldehyde Semicarbazone as a Function of Metal Ion Concentration. [NBS] = 1×10⁻² M, pH = 6.89.

Cu(II) Concentration (M)	% E
1 x 10 ⁻³	57.73
2 x 10 ⁻³	55.10
3 x 10 ⁻³	54.10
5 x 10 ⁻³	55.40

Table-4: Extraction of Co(II) with 4-Nitrobenzaldehyde Semicarbazone as a Function of Metal Ion Concentration. [NBS] = 1×10⁻² M, pH = 6.89

Co(II) Concentration (M)	% E
1 x 10 ⁻³	45.35
2 x 10 ⁻³	44.50
3 x 10 ⁻³	43.50
5 x 10 ⁻³	40.20

CONCLUSION

Studies carried out on the extraction behaviour of Cu(II) and Co(II) using 4-nitrobenzaldehydesemicarbazone at various pH. The extraction was found to be more at pH 6.89. Therefore, further studies such as the effect of metal ion concentration and the extractant on the extraction of Cu(II) and Co(II) were carried out at pH 6.89 to obtain the optimum conditions. The effect of diluents on the extraction was not possible to study because of the insufficient solubility of the 4-nitrobenzaldehydesemicarbazone.

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