



Preparation, Characterization and Evaluation of Extraction Efficiency of N-p-tolyl-N benzohydroxamic Acid towards Certain Metal Ions

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Authors' contributions

This work was carried out in collaboration between both authors. Author NYE designed the study, performed the statistical analysis, wrote the protocol and wrote the manuscript. Author EAA supervisor. Both authors read and approved the final manuscript.

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ABSTRACT

The hydroxamic acid was prepared by the partial reduction of p- nitro toluene to give N-p-tolyl hydroxyl amine which was coupled with benzoyl chloride to give N-p-tolyl-N-benzohydroxamic acid. The hydroxamic acid prepared was identified by their characteristic colored reaction with vanadium (V) and iron (III), melting point, I.R. spectra, ¹H NMR and mass spectrometry. The extractive properties of hydroxamic acids towards the metal ions like Fe (III), Cu (II), Ni (II) and Co (II) were examined using appropriate organic solvent. N-p- tolyl -N-benzohydroxamic acid was found to have a maximum extraction for Fe (III) 75.10% at pH 5.0, Cu (II) 99.81% at pH 5.0, Ni (II) 59.45% at pH 7.0 and Co (II) 99.40% at pH 10.0. The hydroxamic acid was found to extract efficiently metals like Ni (II) in neutral pH values, Fe (III), Cu (II), in pH near to neutral and Co (II) at alkali pH values.

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1. INTRODUCTION

The chemistry of the hydroxamic acids, R-C -NH OH, began in 1869 when W- Lossen, isolated oxalohydroxamic acid from the reaction product of ethyl oxalate and hydroxyl amine.

Later W-Lossen obtained a mixture of mono-, di- and tri- benzoyl derivatives from the reaction of hydroxyl amine with benzoyl chloride [1].

Hydroxamic acid is the name given to N-acyl or aryl derivatives of hydroxylamine. They can be classified as primary, secondary and cyclic. Muzukami, S and Nagata, K (1968) replaced the oxygen donor atom of hydroxamic acids by sulfur atom to get thiohydroxamic acids [2].

Hydroxamic acids are white or light yellow solids, except iodo- and cinnamo- substituted which are pink and light yellow respectively [3]. They are soluble in chloroform, hot benzene, diethyl ether, dioxane and ethanol, sparingly soluble in carbon tetrachloride and cold benzene, and insoluble in water; they are of low melting point [4].

Hydroxamic acids are very weak acids, although they are several times stronger than phenol [5]. The monohydroxamic acids have been prepared by many methods. The most general is the reaction between an ester and hydroxylamine [6]. The other methods have limited application like the reaction of acid anhydride, carboxylic acid, acid chloride [7] and amides [8] with hydroxylamine.

The most important uses of hydroxamic acids are their application as analytical reagents for gravimetric analysis, solvent extraction and spectrophotometric determination of metals [9]. They are also finding wide uses in the analysis of trace metal by flow injection analysis and high performance liquid chromatography. They used also as colorimetric reagents due to the formation of complexes with intensive colors with many metal ions under controlled pH, also they are used in qualitative organic analysis, and since, they form complexes with metal ions they found application in complexometric titration. Also they used in biochemical processes [10].

Solvent extraction or liquid - liquid extraction is a technique in which a solution (usually aqueous) is brought in to contact with a second solvent (usually organic), essentially immiscible with the

first. In the case of inorganic solutes we are concerned largely with samples in aqueous solution so that it is necessary to produce substances, such as neutral metal chelates and ion – association complexes, which are capable of extraction in to organic solvent [11].

The efficiency of extraction depends on the magnitude of D (distribution ratio) and on the relative volumes of liquid phases. The percentage extracted (%E) is given by:

$$\%E = \frac{100D}{\{D + (V_{aq}/V_{org})\}}$$

Where:

V_{aq} : the volume of aqueous layer

V_{org} :the volume of organic layer

Thus the percentage of extraction varies with the volume ratio of the two phases and the distribution ratio.

In this study N-p-tolyl-N-benzohydroxamic acid was prepared and their extraction efficiency was investigated toward certain metal cations at different pH.

2. MATERIALS AND METHODS

2.1 Instruments Used

1. pH meter, jenway , Model 3030.
2. Mettler, melting-point determination apparatus.
3. U.V – Vis spectrophotometer, Perkin Elmer 550s.
4. I.R. spectrophotometer, FTIR – 8400 S, Shimadzu.
5. Atomic absorption spectrophotometer, Shimadzu, model 6800.
6. N.M.R. spectrophotometer, ^1H and ^{13}C were recorded at 400 and 75 MHz respectively, on a Bruker AV – 400 Spectrometer (USA). Chemical shift for ^1H and ^{13}C spectrum were recorded in ppm relative to residual proton of CDCl_3 (^1H 7.28, ^{13}C 77ppm).
7. UHR mass spectrophotometer, Bruker, Maxis 4 G.

2.2 Reagents

Reagents and chemicals used for preparation of N-p-tolyl-N-benzo hydroxamic acid were deionized water, analytical reagents grade (ammonium chloride, sodium hydrogen

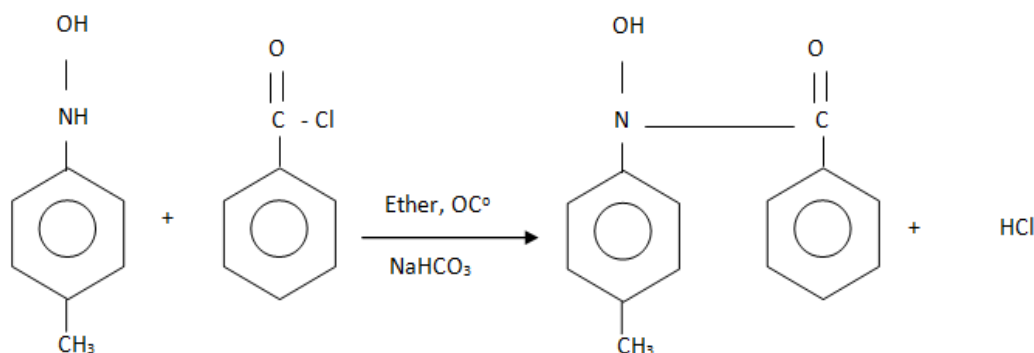
carbonate, p- nitro toluene, diethyl ether and petroleum ether) and general purpose reagents (Zinc dust and Benzoyl chloride).

For preparation of standard metals solutions all reagent are A.R. Grade. The reagents used were ammonium iron (III) sulfate dodecahydrate, Copper sulfate pentahydrate, Nickel sulfate and Cobalt chloride.

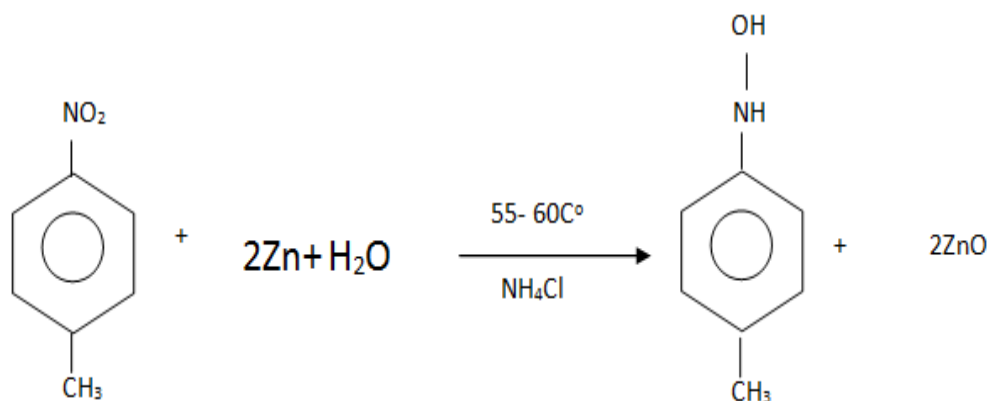
Buffer 1 to 10 were prepared. All buffers prepared were checked with a pH meter and adjusted to the required pH with few drops of either dilute hydrochloric acid or sodium hydroxide solution [12,13].

2.3 Preparation of N-p-tolyl-N-benzo hydroxamic acid

This ligand was prepared by the coupling reaction of N-P-tolyl hydroxyl amine and benzoyl chloride according to the equation:



Scheme 1 Preparation of N-p-tolyl-N-benzo hydroxamic acid



Scheme 2 Preparation of N-p-tolyl hydroxyl amine

The percentage yield 30 g (60.98%). The melting point 93°C (lit. m.p. 93°C) [14]

2.3.1 Preparation of N-p-tolyl hydroxyl amine

54.8 g (0.4mole) of p-nitro toluene, 800 cm³ of water and 25 g (0.4mole) of ammonium chloride were placed in a two liter beaker equipped with a thermometer and mechanical stirrer. The mixture was stirred vigorously; 59.5 g (0.9mole) of zinc powder were added during about 15 minutes. The rate of addition was controlled by the temperature was raised to 55-60°C and kept in this range until all zinc had been added. The stirring continued for 15 minutes, by which time the reaction was completed as shown by the fact that the temperature commenced to fall. The warm mixture was filtered to remove the zinc oxide, and washed with 100 cm³ hot water. The filtrate was placed in a conical flask, saturated with sodium chloride and was cooled in an ice bath for one hour to ensues the maximum crystallization of the product. The pale yellow crystals were filtered. The product, N-p-tolyl hydroxyl amine was formed according to the equation:

2.3.2 Coupling of N-p-tolyl hydroxyl amine and benzoyl chloride

12.3 g (0.1 mole) of freshly prepared N-p-tolyl hydroxyl amine as prepared in (2.3.1) was dissolved in 150 cm³ of diethyl ether and filtered. The filtrate was cooled; a little suspension of sodium hydrogen carbonate in water was added. The mixture was stirred vigorously using a mechanical stirrer. (0.1 mole) of benzoyl chloride was dissolved in 100 cm³ of diethyl ether and placed in a separatory funnel and added dropwise to the reaction mixture during a course of an hour. A yellowish white solid was obtained, which was filtered off and washed with water. The filtrate was placed in a separatory funnel and the ether layer was separated and evaporated under vacuum. Any solid matter was added to the product. The product was placed in a beaker and stirred mechanically for 30 minutes with 100cm³ of 10% sodium hydrogen carbonate to remove unreacted acid chloride. The product washed with cold water, and dried. This product consisting of a mixture of mono- and disubstituted derivatives. Mono- substituted N-p-tolyl-N-benzohydroxamic acid was separated from the disubstituted derivatives by extracting it with aqueous ammonia in which only the monosubstituted derivative dissolved. Then filtered and washed. To the filtrate sulphuric acid was added to neutralize and precipitate the acid. The precipitate was filtered and recrystallized from a mixture of petroleum ether (40-60°C) and benzene yield 13.7 g (60%) [15,16].

2.4 Extraction of Metal Ions

2.4.1 General extraction procedure

First the metal stock solution (1000 ppm) was diluted to a reasonably extractable concentration (100 ppm). Then an aliquot of 5 cm³ portions from the diluted metal standard were transferred to six or seven, 25 cm³ volumetric flasks and diluted to the mark with buffer solutions (selected range).

The solutions were transferred quantitatively to six or seven 100 cm³ separatory funnel. 25 cm³, portions of 2x10⁻² M hydroxamic acid dissolved in organic solvent (chloroform) were added to each separatory funnel.

The mixtures were shaken gently for two minutes and then allowed to separate. The aqueous layers (A) were separated in 25 cm³ volumetric flasks, and analyzed for the percentage of metal unextracted by the hydroxamic acid.

3. RESULTS AND DISCUSSIONS

3.1 Characterization of N-P-tolyl-N-benzohydroxamic Acid

Hydroxamic acid was prepared by many methods, but the coupling reaction between the substituted acid chloride and hydroxylamine under cold ether process, was found to be more applicable than the aqueous process, due to the relative purity of the final product obtained which is mainly the monohydroxamic acid.

The hydroxamic acid prepared has white color. Its sparingly soluble in water but are readily soluble in benzene, alcohol and chloroform. Also, it was quantitatively identified by their reaction towards ferric chloride and vanadium (v) solution, giving blood-red and a deep- violet color respectively in the chloroform extract. The melting point was found 113°C.

The hydroxamic acid prepared show the most characteristic bands using I.R. spectrophotometer (Fig. 1). 3107.11cm⁻¹ for(-OH), 1635.52cm⁻¹ for (C=O), and 918.05cm⁻¹ for (N – O).

The mass spectrum of N-p-tolyl-N-benzohydroxamic acid gave the correct molecular weight (227) and fragments sequence of 122.0364, 150.0314 and 226.1004, corresponding to C₆H₅CH₃.NOH, C₆H₄CH₃.NOH.CO and (M – H) respectively (Fig. 2).

The ¹H NMR spectra of hydroxamic acid under investigation show the characteristic of the proton of the hydroxyl group attached to the nitrogen atom (Fig. 3) in the region 9.113 ppm. The shifting of the resonance signal of hydroxyl proton to lower field supports intermolecular hydrogen bonding. The protons of aromatic ring appear in the region 7.12-7.459 ppm. The protons of – CH₃ group appear in the region 2.346 ppm.

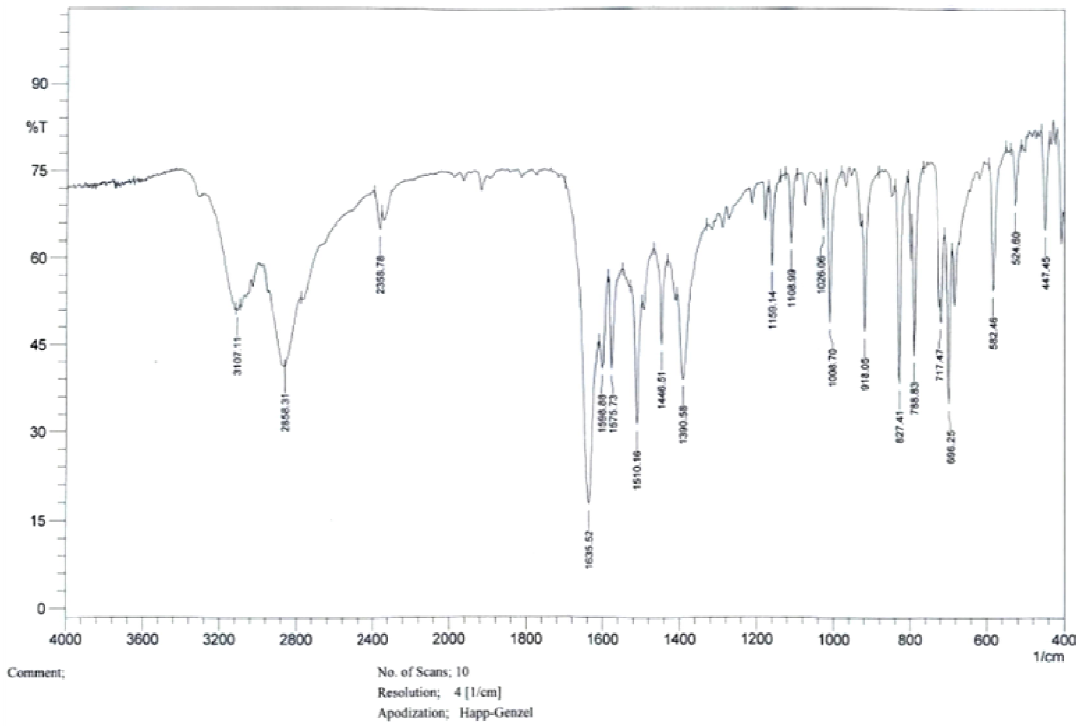


Fig. 1. I.R spectrum of N-P-tolyl –N-benzo hydroxmic acid

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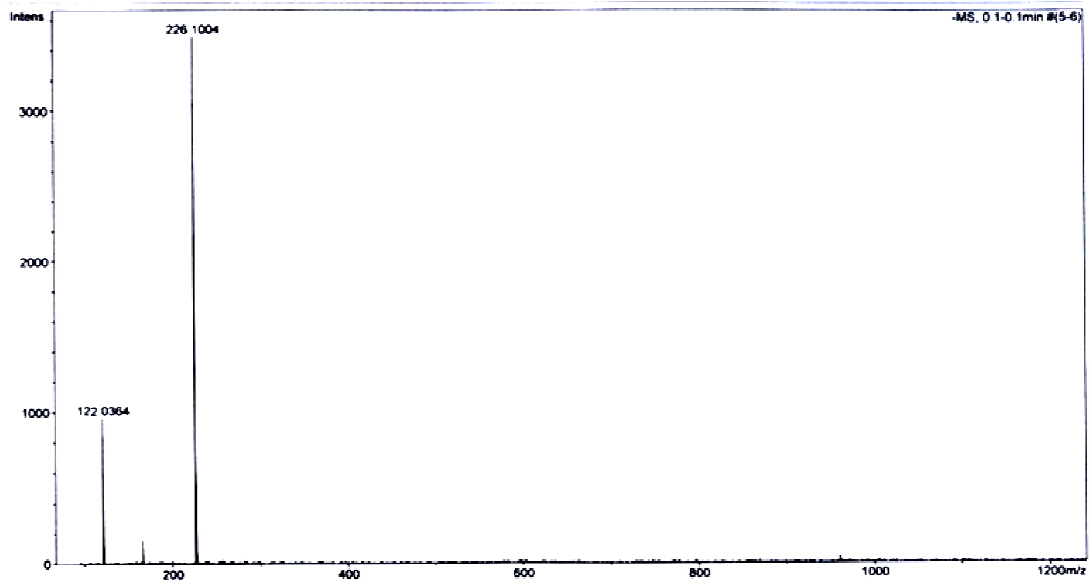


Fig. 2. Mass spectrum of N-P-tolyl –N-benzo hydroxmic acid

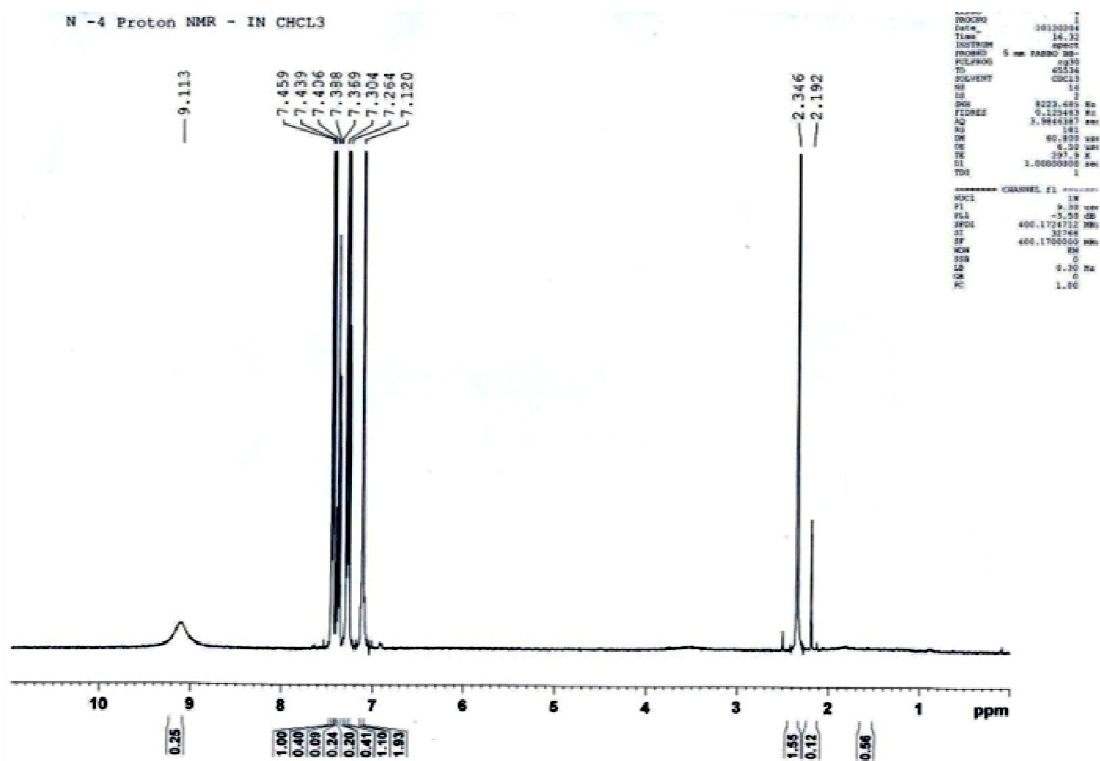


Fig. 3. ¹H NMR spectrum of N-P-tolyl –N-benzo hydroxamic acid

3.2 Analysis for Metal Ions Content Using AAS

Standards of Fe (III), Cu (II), Co (II), and Ni (II) were sprayed first in the atomic absorption spectrophotometer to calibrate the instrument, and then followed by the extracted aqueous layers (A).

The extractability of the substituted hydroxamic acid, as with other chelating agents which are weak acids, indicates a general increase of the amount of metal extracted with an increase in pH.

3.2.1 Iron (III)

Iron (III) in acidic media form blood- red chelate complexes with hydroxamic acid prepared. The maximum extraction of the hydroxamic acid at pH 5.0.

3.2.2 Copper (II)

The recovery of Cu (II) by the hydroxamic acid studied is complete at pH 5.

The high percentage of extraction can be explained according to the acidity of hydroxamic acid prepared and stability of Cu (II) to form quite stable complexes as shown in Irving – William series.

Mn (II) < Fe (II) < Co (II) < Ni (II) < Cu (II) < Zn (II)

3.2.3 Nickel (II)

The hydroxamic acid prepared have the extraction maximum for Ni (II) at pH 7.0. The low recovery due to methyl group at the para- position which decreased the acidity of the molecule and extraction of metals.

3.2.4 Cobalt (II)

Cobalt (II) extraction is very low at low pH with the hydroxamic acid prepared. The percentage of extraction increases with an increase in pH.

The maximum percentage of extraction of Co (II) with the hydroxamic acid is at pH 10. The high percentage of extraction due to the acidity of hydroxamic acids prepared and cobalt (II) which formed stable complexes according to Irving – William series.

Table 1. Result of extraction of Fe (III) with N-p-tolyl-N-benzohydroxamic acid

pH	Conc. of A (ppm)	%Unextracted	%Extracted
1	16.8654	84.30	15.70
2	10.4454	52.20	47.80
3	8.9475	44.70	55.30
4	7.3219	36.60	63.40
5	4.9706	24.90	75.10
6	8.6373	43.20	56.80

Table 2. Result of extraction of Cu (II) with N-p-tolyl-N-benzohydroxamic acid

pH	Conc. of A (ppm)	%Unextracted	%Extracted
1	14.2040	71.00	29.00
2	0.7944	4.00	96.00
3	0.1541	0.80	99.20
4	0.1234	0.60	99.40
5	0.0472	0.20	99.80
6	0.1347	0.70	99.30
7	0.3613	1.80	98.20

Table 3. Result of extraction of Ni (II) with N-p-tolyl-N-benzohydroxamic acid

pH	Conc. Of A (ppm)	%Unextracted	%Extracted
1	16.3150	81.60	18.40
2	18.1600	90.80	9.20
3	17.1900	86.00	14.00
4	16.5400	82.70	17.30
5	12.9700	64.85	35.15
6	15.0800	75.40	24.60
7	8.1100	40.55	59.45

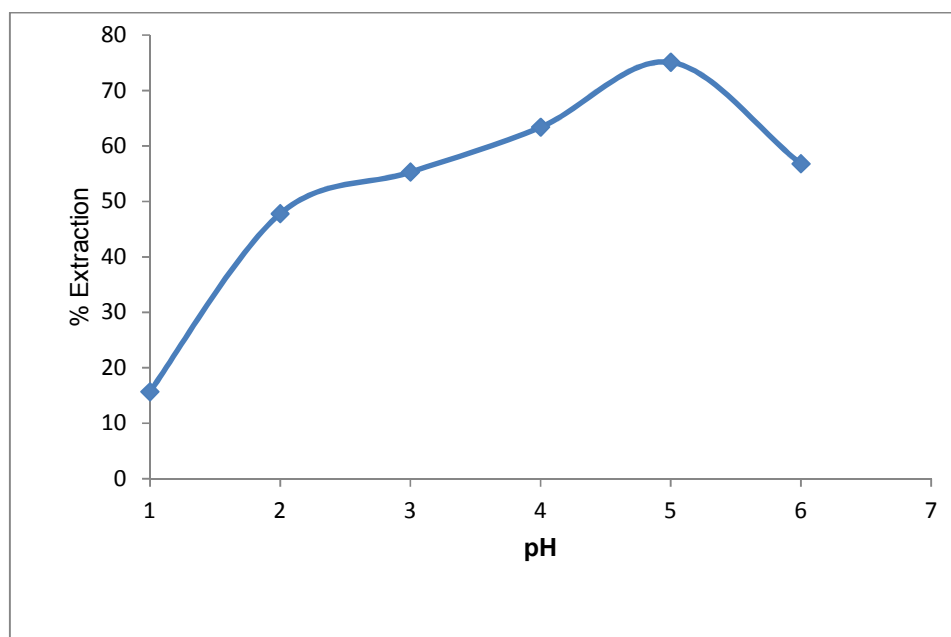


Fig. 4. Extraction curve showing distribution of Fe (III) as a function of pH for N-p-tolyl-N-benzohydroxamic acid

Table 4. Result of extraction of Co (II) with N-p-tolyl-N-benzohydroxamic acid

pH	Conc. of A (ppm)	%Unextracted	%Extracted
4	18.7317	93.70	06.30
5	16.0710	80.40	19.60
6	14.6088	73.00	27.00
7	12.8870	64.40	35.60
8	7.4360	37.20	62.80
9	0.9820	4.90	95.10
10	0.1133	0.60	99.40

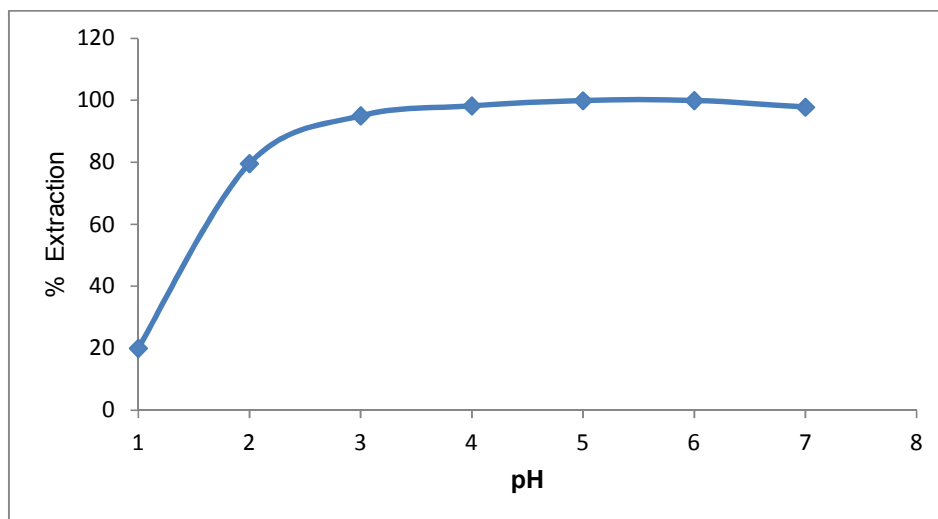


Fig. 5. Extraction curve showing distribution of Cu (II) as a function of pH for N-p-tolyl-N-benzohydroxamic acid

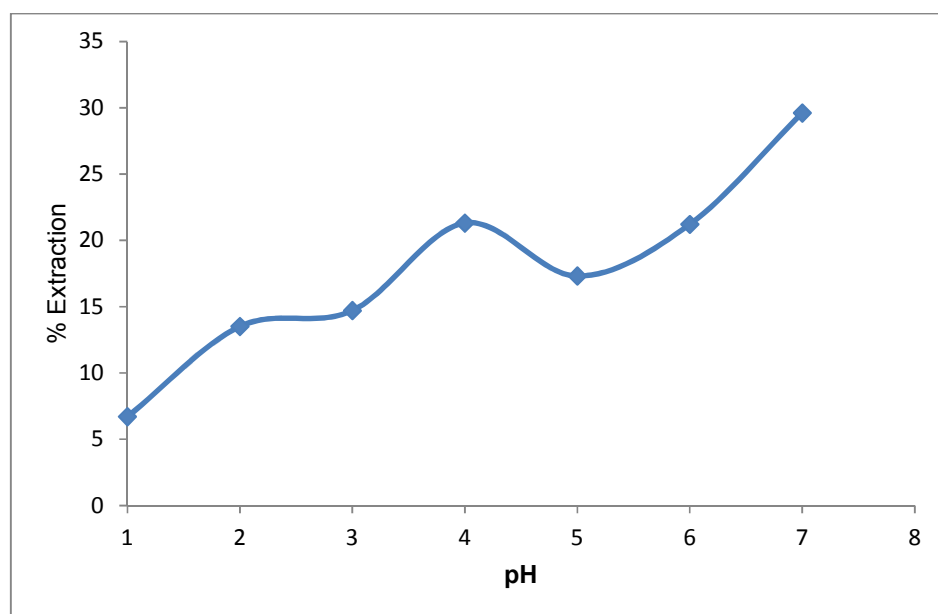


Fig. 6. Extraction curve showing distribution of Ni (II) as a function of pH for N-phenyl-N-p-nitrobenzohydroxamic acid

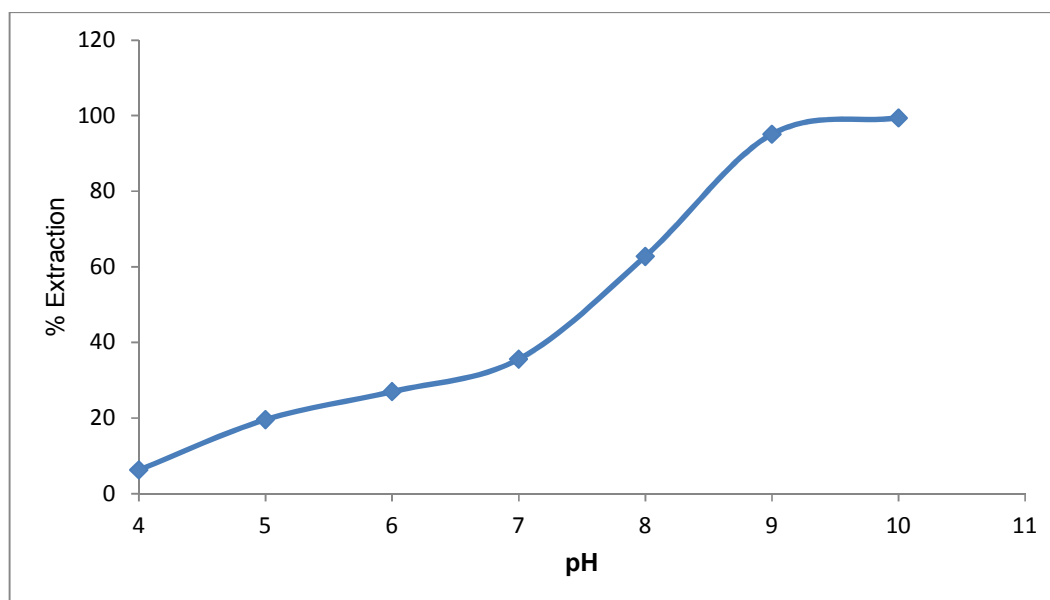


Fig. 7. Extraction curve showing distribution of Co (II) as a function of pH for N-p-tolyl-N-benzohydroxamic acid

4. CONCLUSION

Hydroxamic acids find a number of applications in chemistry, biology and medicine due to their large roles as chelating agents, inhibitors of various enzymes, anticancer, antifungal and many other uses. In this paper, we reported the synthesis of N-p-tolyl-N-benzohydroxamic acid and their extraction efficiency towards certain metal ions. The synthesized hydroxamic acid was characterized using I.R., ^1H NMR and mass spectroscopy.

The extraction power of the synthesized hydroxamic acid were examined toward certain metal ions and it found that the extraction power increased with increasing pH.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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