



Scholars Research Library

Archives of Applied Science Research, 2016, 8 (8):31-36
(<http://scholarsresearchlibrary.com/archive.html>)



A Study on spectrophotometric determination of copper from wastewater and its removal using magnetite Nanoparticles

K. P. Satheesh¹ and V. Suryanarayana Rao²

¹Department of Chemistry, Gates Institute of Technology, Approved by AICTE & Affiliated to JNTUA- NH-44, Gooty anantapuram (v), Peddavaduguru (M), Gooty, pin-515401, Anantpur Dist, [A.P.]

²Department of Chemistry, Sri Krishnadevaraya University, Anantapur-515 003. [A.P.]

ABSTRACT

Heavy metals can be hazardous even at very low concentrations. When they get in to water supplies and aqueous environments the health of plants and animals as well as humans can be impaired. Heavy or toxic metals such as cadmium Cd (II) Nickel Ni(II) Copper Cu (II) Lead Pb(II) and Bismuth Bi(III) are trace metals with a density at least five times that of water. As such they are stable elements and they cannot be metabolized by the body and bioaccumulative. Toxic metals are commonly found in waste water and removing them efficiently presents a unique challenge.in the present study the author has developed an organic reagent “4-HydroxyBenzaldehydethosemicarbazone” and studied the complexation reaction between Cu (II) and 4-HBTS spectrophotometrically. The data pertaining to these studies reveals that Cu (II) shows favorable conditions for complex formation under weak acidic condition (P^H - 5-6) . The results showed that the metal ions can be determined quantitatively in μg quantities using the standard procedures. The suitability of this method for the determination of copper in the range is 0.127-1.27 $\mu\text{g/ml}$. The above mentioned method has been extended for the determination of Cu (II) present in wastewater sample. The author has compared the present method with other spectrophotometric methods for the determination of copper. A review on removal of Cu (II) from the waste water sample using magnetite nanoparticles is presented in this pper.

Key words: wastewater, heavy metals, aqueous environment, 4-HBTS, Complexation, Spectrophotometry, pH .Magnetite, nanoparticles.

INTRODUCTION

Thiosemicarbazones are good analytical reagents [1-5]. Copper is an important element in industry and biological chemistry. The human adult requirement is 2 mg per day, and adult human body contains 100-150 mg of copper. Copper is essential for mammal, they become hazardous when present in excess. An excessive accumulation of copper in liver, kidney and brain, leads to liver and kidney failure and various neurological abnormalities. In plants copper reduces chlorophyll content. In this present study a simple, selective and sensitive spectrophotometric method was developed for the determination of copper in water, industrial waste water. Several thiosemicarbazones have been employed as chromogenic reagents for the spectrophotometric determination of copper [6-10]. Development of novel and cost effective nanomaterials for environmental remediation, pollution detection and other applications has attracted considerable attention .Recent advances suggest that many of the issues involving water quality could be resolved using nanoparticles, nanofiltration or other products resulting from nanotechnology [11-

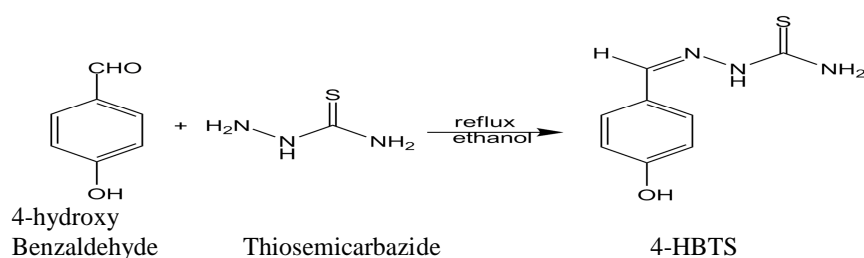
12]. The use of magnetite nanoparticles as adsorbents in water treatment provides a convenient approach for separating and removal of copper by applying external magnetic fields..

MATERIALS AND METHODS

The absorbance and pH measurements were made on a Shimadzu UV-Visible spectrophotometer (model UV-160A) fitted with 1.0cm quartz cells and Elico digital pH meter (modellI20) respectively.

Preparation and characterization of 4-hydroxy benzaldehyde thiosemicarbazone

The reagent was prepared by simple condensation of 1 mole of 4-hydroxy-benzaldehyde(1.22gm) with 1-mole (0.92gm) of thiosemicarbazide in a clean 250ml round bottomed flask 4-hydroxybenzaldehyde was dissolved in 100ml of methanol and thiosemicarbazide was dissolved in hot water. The solutions were mixed and refluxed for two hours. On cooling brown colored product was formed which was collected by filtration. It was recrystallized using methanol and dried in vacuum.



The yield was 80% by weight. and the M.P. is 207-209⁰C. The structure of the compound was established using IR spectra and NMR spectra,

Characterization:

The IR spectrum of the compound was recorded using Perkin-Elmer 137 IR spectrometer in KBr. The peaks observed at 3458cm⁻¹ and 3342⁻¹ may be assigned to symmetric and assymetric (-N-H) stretching frequency of primary amino group. The peak observed at 3028cm⁻¹ may be assigned to Ar-H stretching frequency of aromatic proton, and that observed at 1595cm⁻¹ to C=N stretching frequency of azomethine. The peak observed at 3218-3092 for -OH group. A strong peak observed at 1056cm⁻¹ may be assigned to C=S stretching frequency. The peaks observed in the range of 1530-1360cm⁻¹frequency were charecteristic aromatic ring stretching frequency.

The ¹H-NMR spectrum of the compound was recorded with DRX300 NMR spectrometer in DMF solvent. The peak observed at δ value 10.74(H) was charecterstic of phenolic -OH group. The peak found at δ value 7.86(4H) may be due to aromatic protons, the peak observed at δ value 6.8 (2H) may be due to -NH₂ protons attached to thionylgroup (C=S) and the peak observed at δ value 9.0 is due to aldehydic proton. The peak at δ value 11.5 may be due to -NH proton (azomethine).

Preparation of the solutions:

Cu (II) solution

Stock solution of copper sulphate (1 x 10⁻² M) was prepared from 0.6242 g CuSO₄ (AR, BDH) with doubly distilled water and made upto 250 ml. The stock solution was standardised. The stock solution was suitably diluted to get the required concentration.

Stock solution of the reagent

0.195 g of recrystallised sample of the reagent 4-hydroxybenzaldehyde thiosemicarbazone was dissolved in DMF in a 100 ml volumetric flask to obtain the stock solution (0.1 M), and it was suitably diluted to get the required concentration. Fresh reagent solutions were prepared as and when required.

Buffer solutions

The buffer solutions are prepared by mixing 1M hydrochloric acid and 1M Sodium acetate (pH 1.0-3.0) and 0.2M acetic acid and 0.2M sodium acetate (pH 3.5-7.0). Exact pH of the solution was measured using a pH meter

RESULTS AND DISCUSSION

Cu (II) reacts with 4-HBTS in weak acidic pH to give a green coloured water soluble species. The colour reaction between Cu (II) and 4-HBTS is instantaneous even at room temperature. The maximum absorbance λ_{\max} of the green coloured species (complex) was observed at 370nm which remains constant for 24 hours. Studies on the effect of pH on the absorbance revealed that the maximum colour was formed in a solution of pH 6.5. The studies relating to the effect of Cu (II) revealed that a linear relationship exists between metal ion concentration and the absorbance in the range 0.06354-1.272 μ g/ml. The molar absorptivity and sandell's sensitivity are $2.85 \times 10^4 \text{ L.mol}^{-1} \text{ cm}^{-1}$ and $2.23 \times 10^{-3} \mu\text{g} / \text{cm}^2$ respectively. The effect of the reagent on absorbance is also studied, no linear relationship is found between the reagent and the absorbance. As the metal ion Cu (II) forms a coloured complex with reagent, an attempt is made to determine the composition and the stability of the complex. Job's method and mole ratio method are conducted to make these determinations. It is noticed that Cu(II) forms a stable green coloured 1:2 [M:L] complex with 4-hydroxy benzaldehyde thiosemicarbazone. The stability complex was found to be 5.93×10^{10} . Data related various parameters of Cu (II)-4HBTS complex is presented in table-1.

Table-1: physico-chemical and analytical characteristics of Cu(II)- 4HBTS

Characteristics	Results
λ_{\max} (nm)	370
p ^H range (optimum)	4.0-6.5
Moles of the reagent required per mole of metal ion for complete colour development	10 folds
Molar absorptivity ($\text{L.mol}^{-1} \text{ cm}^{-1}$)	$2.85 \times 10^4 \text{ L.mol}^{-1} \text{ cm}^{-1}$
Sandell's sensitivity ($\mu\text{g}/\text{cm}^2$)	2.23×10^{-3}
Standard deviation in the determination of 1.27 μ g/ml of Cu(II) for ten determinations.	0.000324
RSD	0.025%
Regression equation	$A_{370} = 0.0295 C + 0.0458$.
Beer's law validity range ($\mu\text{g}/\text{ml}$)	0.06354-1.272
Composition of the complex (M:L) obtained in job's and mole ratio method.	1:2
Stability constant	5.93×10^{10}

The author has compared the present method with other spectrophotometric methods for the determination of copper anumarised in table-2.

Applications of the proposed method:

To confirm the usefulness of the proposed method, it was applied to the determination of copper in ground water and in industrial waste water samples. For this purpose the water samples were collected from different parts of industrial estate. The water samples [1liter] were collected in clean 2 liter beakers and slowly evaporated to 25mL; then 5ml of H₂O₂ was added and evaporated to dryness. It was then dissolved in 20mL of water and filtered to remove insoluble substance. The filtrate was collected in 100mL volumetric flask quantitatively and diluted to the mark with distilled water. Two untreated waste water samples collected from different parts of industrial estate have been analyzed after treating the water sample using the procedure described above. Reliability of the method was checked by the spiking experiments and comparing the results with the data obtained by GF- AAS as shown in the table- 3, the results obtained with the proposed method agree well with data obtained by furnace atomic absorption analysis and the recovery of the spiked sample is good, suggesting that the procedure is reliable for sample examination.

Table 2: Comparison of the present method with other spectrophotometric methods for the determination of copper

Reagent	$\lambda_{\text{max}}/\text{nm}$	Optimum pH range	Beer's law validity range ppm	Molar absorptivity $\text{L mol}^{-1}\text{cm}^{-1}$	M:L ^a	Remarks	Ref.
2,7-Dichloroquinoline-3-carbaldehyde thio-semicarbazone	406	6	0.003	1843.5	-----	Many metal ions interfere and poor sensitivity	[11]
8-methoxy-2-chloro quinoline-3-carbaldehyde thiosemicarbazone	410	5	3	0.0026768	1:1	Many metal ions interfere and poor sensitivity	[12]
Salicylaldehyde thiosemicarbazone	375	6.5-7.5	0.5-6.0	9200	1:1	Fe(II), Co(II), Zn(II),V(V), Bi(III) Cd(II) and thiocyanate interfere , less sensitive	[13]
7-Methyl-2-chloroquinoline-3-carbaldehyde thiosemicarbazone	400	4.0	5.0	343.4	-----	Mo (IV) interfere less sensitive	[14]
Picoline aldehyde 4-phenyl-3-thiosemicarbazone	413	-----	2.0-30	16000	-----	Ag(I), Au(II) and Pt(IV) interfere, less sensitive	[15]
5,5'-Dimethyl-1,2,3-cyclohexanetrione-1,2dioxime	383	-----	0-11.2	4600	1:3	Less sensitive	[16]
Pyruvaldehyde (N,N-dibutyl) bis-thio semicarbazone	488	5-12	-----	10,900	1:1	Less sensitive	[17]
2-Carboxybenzaldehyde thiosemicarbazone	346	-----	0.5- 5.0	12,000	1:1	Less sensitive	[18]
2,4-Dihydroxy-5-bromoacetophenone thiosemicarbazide	420	6.0	12.7	1459	1:1	Poor sensitivity	[19]
Benzaldehyde-4-(2-hydr oxy -5-sulphonyl 3-thiosemicarbazone	325	4.5	7.62	744	1:2	Very poor sensitivity	[20]
4-Chloroisoinitroso acetophenone thiosemicarbazone.	400	7.5-8.5	0.2-20	2518	1:2	Ag(I), Co(II),Pb(II),Cd(II)Cyanide,Tartarate and Ni(II), EDTA interfere, less sensitive	[21]
4-hydroxy benzaldehyde thio semicarbazone	370	6.5	0.06354-1.272	16347	1:2	Highly sensitive	P.M ^b

: a. Metal ligand. b. Present method

Table-3: Determination of copper in ground water and in industrial waste water samples

Sample	Added $\mu\text{g/mL}$	found $\mu\text{g/mL}$	Recovery %	GF-AAS $\mu\text{g/mL}$
Ground water	15.0	ND ^b 14.7 \pm 0.3	98.7	5.3 \pm 0.2
Industrial Waste wter (1)	15.0	76.2 \pm 0.8 90.6 \pm 1.3	96	75.6 \pm 1.8
Industrial waste water(2)	15.0	68.3 \pm 1.2 82.5 \pm 1.4	94	67.8 \pm 1.2

^a mean and standard deviation of three determinations, ^bND – not determined.**Application of magnetite nanoparticles for heavy metal removal from waste water:**

Development of novel and cost effective nanomaterials for environmental remediation, pollution detection and other applications has attracted considered attention . Recent advances suggest that many of these issues involving water quality could be resolved or greatly ameliorated using nanoparticles, nanofiltration or other products resulting from the development of nanotechnology (22-23).

Toxic metal ions Cr (III) ,Co (II), Ni(II) , Cu (II), Cd (II), Pb (II) and bacterial pathogens (Escherichia coil) from water were removed by magnetite nanoparticles functionalized with carboxyl (Succinic acid) , amine (ethylene diamine) and thiol (2,3-dimercaptosuccinic acid) groups. These nanoparticles were prepared by Singh et al (24).

carboxy methyl- β -cyclodextrin modified Fe_3O_4 nano particles (CM β CD-MNPs) were synthesised and used for removal of copper ions from aqueous solution by Badruddoza et al. (25). The characteristics results of FTIR, TEM, TGA and XPS show that CM- β -CD is grafted on to Fe_3O_4 nanoparticles. The grafted CM- β -CD on the Fe_3O_4 nanoparticles contributes to an enhancement of the adsorption capacity because of the strong abilities of the multiple hydroxyl and carboxyl groups in CM- β -CD to absorb metal ions. The adsorption of Cu (II) on to CMCD-MNPs was found to be dependent on pH and temperature. The thermodynamic parameters reveal the feasibility, spontaneity and

exothermic nature of the adsorption process. FTIR and XPS reveal that Cu (II) adsorption on to CMCD-MNPs mainly involves the oxygen atoms in CM-β-CD to form surface complexes. In addition, the copper ions can be desorbed from CMCD-MNPs by citric acid solution with 96.2% desorption efficiency and the CMCD-MNPs exhibit good recyclability.

The development of humic acid (HA) coated Fe₃O₄ nanoparticles (Fe₃O₄/HA) by Lieu et al.(26) were used for the removal of toxic cations such as Hg (II),Pb (II), Cd (II) and Cu(II) from water. Fe₃O₄/HA were prepared by the co-precipitation method. TOC and XPS analyses showed that the as prepared Fe₃O₄/HA contains ~ 11 % (w/w) of HA fractions abundant in O and N-based functional groups. TEM images and laser particle size analysis revealed the Fe₃O₄/HA (WITH ~ 10nm Fe₃O₄ cores) aggregated in aqueous suspensions to form aggregates with an average hydrodynamic size of ~ 140nm. Sorption of the heavy metals to Fe₃O₄/HA reached equilibrium in less than 15 minutes and agreed well to the Langmuir adsorption model with maximum adsorption capacities ranging from 45 to 100mg/g. The Fe₃O₄/HA was able to remove over 99% of Hg(II) and Pb(II) and over 95% of Cu (II) and Cd (II) in natural and waste water at optimized pH.

CONCLUSION

In this study it was shown that Thiosemicarbazones could be used as a ligand for the Spectrophotometric determination of copper metal ions. The methods described in this paper are applicable for the rapid, precise and reliable determination of trace amounts of Copper in water and in industrial waste water. The present method is compared with other spectrophotometric methods for the estimation of copper. The use of magnetite nanoparticles as adsorbents in waste water treatment provides a convenient approach for separating and removing the heavy metals from waste water. Among the main advantages of these nanomaterials is the possibility of surface modifications with different organic or inorganic coating agents to allow the removal of a wide range of heavy metals with specificity. However, the application of these methods is still limited in the early stage and more research in the field is certainly necessary.

REFERENCES

- [1] Smita Nigam, Patel and Arabinda Ray, *Synth. Reat. Inorg. Met-Org. Chem.*, **1998**;28(7);1187-1205
- [2] K.Hussain Reddy, P.Sambasiva Reddy, and P.Ravindra Babu., *J. Inorg.Biochem*, **1999**; 7; 169-176.
- [3] Noriko Chikarashi Kasuga, Kiyoshi Sekino, Chisa Koumo, Nobuhiro Simada, Motokoi Ishikawa and Kenji Nomiya. *J.Inorg.Biochem*, **2001**;84;55-65
- [4] Javier Garcia-Tojal, Jose Luis Pizarro, Africa Garcia-orad, Ana Rocio Peroz-saz, Maria Ugalde, Antonia Alvarezdiaz, Jaun Luis Serra, Maria Isabel Arriortua and Teofilo Roio, *J.Inorg.Biochem*, **2001**,86,627-633.
- [5] EI Mostapha Jouad, Amedeerio, Magali Allian, Mustayeen A.Khan and Gilles M.Bouet, *Polyhedron* , **2001**,20, 67-69.
- [6] Y.M.Issa, M.M.Omar, M.S.Rizk and S.E. Mohammed, *Ind. J. chem.Sect. A* **1996** ,35A (B),315.
- [7] Tojal Javier Garcia etal *J. Inorg.Biochem* ,**2001**,84;55.
- [8] Shinde, S. Priyadarshini and P.M.Dhadke *Ind.J.Chem.Technol.*, **1996**, 3(6), 367
- [9] Tarley C.R.T., Santos W. N.L., Antos C.M., Arrude M.A.Z and Ferreira S.L.C., *Anal.lett*, **2004**, 37, 1437.
- [10] Soylak M. Elci L., *Chemia Analityenza (warsaw)* ,**2003**, 48, 77.
- [11] V. A. Jadhav and Mrs. Vandre, *J. Indian Chem. Soc.*, **1992** ,69,791
- [12] V. A. Jadhav and A. G. Vandre, *J. Indian Chem. Soc.*,**1995**, 72, 747
- [13] N. S. Reddy and D. V. Reddy, *Microchem. J.*, **1985**, 31(3),318
- [14] V. A. Jadhav and M. V. Kulkarni, *J. Indian Chem. Soc.*,**1992**, 69, 287.
- [15] K. Uesugi, T. Kusuda, H. Nishioka, T. Kumagai, and T.Nagahiro, Kenkyu Hokoku-Himeji Kogyo Daigaku Kogakubu, **1992**, 45, 1
- [16] R. Salim, A. H. Laila, and A. Qamhich, *Spectrosc. Lett.*,**1988**, 21(7), 541.
- [17] M. Tongsen, L. Meng, H. Congde, L. Kuaizhi, L.Zhenghao, and Z. Daxuesuenao, Ziaru Keruebau, **1999**,31(3), 70.
- [18] P. Lopez-de-Alba, L. Loper-Martinez, and J. Amador- Hernandez, *Bol. Sol Chil Quim*, **1999**, 44(4), 469.
- [19] J. M. Desai and K. K. Desai, *Asian J. Chem.*, **1999**, 11(4),1313.
- [20] A. L. Patel and I. J. Patel, *J. Inst. Chem. (Indian)*, **2000**,72(1), 8.
- [21] R. S. Lokhande, S. V. Poman, and H. R. Kapadi, *Asian J.Chem.*, **2001**, 13(3), 1222.
- [22] J.Schutle and J.Dutta, Nanotechnology in environmental protection and pollution, Science and Technology of advanced materials ,**2005**, 6, 219-220.
- [23] M.Auffan, H.J.Shiply, S.Yeann, A.T.Kan, M.Tomson, J.Rose and J.Y.Bottero, Nanomaterials as adsorbents, in :

M.R.Wiesner, J.Y.Bottero (Eds) , Environmental nano technology: Applications and impacts of Nanomaterials, McGraw-Hill, NeYork **2007**, 371-392.

[24] S.Singh, K.C.Barick and D.Bahadur, *journal of Hazardous materials* **2011**, 192, 1539-1547.

[25] A.Z.M. Badruddoza, A.S.H.Tay, P.Y.Tan, K.Hidajat and M.S. Uddin, *Journal of Hazardous Materials.*,**2011**, 185, 1177-1186.

[26] J.F.Liu, Z.S.Zhao and G.B. Jiang, *Environmental Science & Technology*,**2008**;42, 6949-6954.