Vol III Issue IX March 2014

Impact Factor : 2.2052(UIF)

ISSN No :2231-5063

International Multidisciplinary Research Journal

Golden Research Thoughts

IMPACT FACTOR : 2.2052(UIF)

Welcome to GRT

RNI MAHMUL/2011/38595 **ISSN No.2231-5063**

Golden Research Thoughts Journal is a multidisciplinary research journal, published monthly in English, Hindi & Marathi Language. All research papers submitted to the journal will be double - blind peer reviewed referred by members of the editorial board.Readers will include investigator in universities, research institutes government and industry with research interest in the general subjects.

Address:-Ashok Yakkaldevi 258/34, Raviwar Peth, Solapur - 413 005 Maharashtra, India
Cell : 9595 359 435, Ph No: 02172372010 Email: ayisrj@yahoo.in Website: www.aygrt.isrj.net

Golden Research Thoughts
ISSN 2231-5063
Impact Factor : 2.2052(UIF)
Volume-3 | Issue-9 | March-2014
Available online at www.aygrt.isrj.net

SOLID PHASE EXTRACTION OF CU (II) BY PYRIDINE-2, 6-DIMETHANOL MODIFIED WITH ALUMINA FOR ITS PH DEPENDENT DETERMINATION BY FAAS.

M F Rahman , A. Chakraborty[1] , S. N. Bandyopadhyay[2] and Tanmoy Das[3]

[3]Department of Chemistry, University of Burdwan, Burdwan-713 104, India.
[2]PG Department of Environmental Sciences (Autonomous), Sambalpur University, Odisha, India.
[1]Union Christian Training College, Murshidabad, WB, India

Abstract:-Toxicity and geochemical importance of copper (II) is considered its separation by chelation technique in water samples using Pyridine-2, 6-dimethanol modified with alumina as a chelator. The standard solution of Cu (II) is considered for its analytical parameters as: dependent of pH, amount adsorbent, kinetic study, effect of temperature, interferences of other ions and elution rate. The proposed method is very simple and reliable for the extraction of Cu (II) in different water samples and its relative standard deviation is satisfactory.

Keywords: Solid Phase Extraction, Cu (II) solution, Pyridine-2, 6-dimethanol modified with alumina, 1% HNO_3, FAAS.

INTRODUCTION:

Metal ions-ligands coordination complexes are the intense analytical approach for the determination of metal ions of the environmental samples. Few metal ions are constituents of the biological enzymes and play a vital role in enzymatic metabolism in biological systems, but its toxicity influences to the researchers for direct determination in environmental samples. In this proposed method, for direct determination of Cu (II) at trace level by Flame atomic absorption spectrometry (FAAS) has been extensively used. For the determination of metal ions several separation techniques have been developed. These methods are liquid-liquid extraction, preconcentration, cloud point extraction, co-precipitation, anodic stripping voltametry, on-line solid phase extraction. But solid phase extraction (SPE) methods have some important aspect over the above methods. A large number of solid sorbents are used for the extraction of metal ions and Cu (II) ions also at trace level. These are empore chelating resins disk, neutral polymer Amberlite XAD, Amberlite IR-120, activated carbon, microcrystalline naphthalene, polyurethane foam, octa decyl silica-gel, distosan, Dowex IX8 and Dowex 50WX8, styrene-divinyl benzene, zeolite, cellulose, benzophenone and others.

The above methods have several disadvantages for being time-consuming, samples availability, complexation of metal ions problem, large wastes, and unsatisfactory selection of solvent. These problems are the parts of our great effort to develop an alternate, speedy and less expensive procedure to determine copper (II) ion at trace level in environmental water samples. The proposed method has several advantages in comparison to the others. This method is also effective for the removal of interferences in a simpler way, low sample volume, high recovery and simplicity of the operation.

The pH dependent extraction of metal ions in the complexation chemistry has been studied extensively. This analytical approach encouraged us for the extraction of Cu (II) ion also. In this context, Pyridine-2, 6-dimethanol (PDM) is impregnated with alumina is considered as a selective chelator for the complexation with Cu (II) ion. It is found that extraction of the metal ion occurs at pH=5-6. At this reliable pH, various analytical approaches have been studied in this proposed method. And in all the steps, application of this method was satisfactory.

Experimental:

Reagents and Solutions:

Extra pure methanol, hydrochloric acid, ammonia solution, all from E Merck, Germany, was used. Pyridine-2, 6-dimethanol (Sigma and Aldrich) and neutral solid sorbent alumina was of analytical grade reagent for the determination of the

metal ion from E Merck. All the solutions were prepared using analytical grade reagents. A stock solution of 500ml Cu (II) was prepared by dissolving 0.1208 gm of Cu $(NO_3)_2$.$3H_2O$ in triple distilled and deionized water containing 1% HNO_3.

Instrumentation:

A Systronics digital pH meter (model 335) equipped with a combined glass-calomel electrode was used to monitor the pH of the solutions and a Varian model Specter AA, 55B (Mulgrave, Victoria, Australia) flame absorption spectrometer equipped with a deuterium background corrector for the determination of metal ions. A copper hollow cathode lamp operating at 324.5 nm was used as radiation source. A mechanical shaker (BOD-incubator: YONA Mfg. Indian Instruments Manufacture Co., Kol-12) was used throughout the experiments.

General Procedure:

Impregnation of 2 gm Pyridine-2, 6-dimethnol on the surface of 5.8 gm of alumina beads was prepared at the ratio of 1:2 in methanol solvent and the mixture was shaken by a mechanical shaker at about 500-600 rpm about 30^0 C temperatures. The modified beads of PDM were filtered and it was washed with doubled distilled water, and dried in air. Then, the modified solid sorbent was ready for the determination Cu (II) ion in volume samples. 250 ml of the sample solution containing microgram of Cu (II) in 1% HNO3 was prepared, and from the stock solution of Cu (II), all working solutions of the sample were mixed with solid sorbent. Then, pH was adjusted by liquid ammonia and HCl to optimum values, and the mixture was shaken at 500 rpm by a mechanical shaker at the normal temperature.

The complex was adsorbed on the surface of PDM loaded alumina. Different experimental parameters such as pH, equilibrium time, and effect of temperature and concentration of eluants were studied to optimize the sorption and desorption. The concentration of Cu (II) ions were determined by using flame atomic absorption spectroscopy (FAAS).

RESULTS AND DISCUSSION:

Sorption studies and impregnated resins:

Pyridine-2, 6-dimethanol (PDM) is one of the weak sorption acidic chelating agents. It has been used for the solvent extraction of metal ions, because it has been found to form stable metal ion-ligand complexes. Considering the stability of metal ion – complexes, it undergoes as a suitable modifier for selective extraction and pre-concentration of metal ions. In this proposed method we used PDM as a extracting agent for the selective solid phase extraction and determination of Cu (II) ions by PDM-alumina beads and FAAS. Some experiments were done in order to investigate the quantitative extraction and determination of Cu (II) ions by the modified beads of PDM in the aqueous sample solution containing microgram of copper. It is also found that a non-modified bead of alumina does not retain Cu (II) ions. The test solutions containing 0.01208 gm of Cu (II) in 50 ml were used for all variable optimizations.

Effect of pH:

The influence of pH of test solution on the sorption process was investigated at a pH range of 2.3 to 5.9. The pH was adjusted by liquid NH_3 solution and dil.HCl. The results shown in Fig.1, indicates that the Cu (II) can be retained quantitatively at a pH range of 5 to 6. As it can be found that at low pH, leads to a decrease in the retention of Cu (II) due to the possibility for the protonation of the donor sites of the ligand in acid medium. And at higher pH than 6, probably due to the hydrolysis of Cu (II) ions, extraction efficiency was decreased. Hence pH=5 was preferred throughout the studies.

Kinetic Study:

Extraction duration of the metal ions is one of the most important factors which must be considered. In this regard, at the optimum conditions of all variables in the batch method, 50 ml of 3.027 mg L- Cu (II) ion was shaken with 200 mg of modified beads at the ambient temperature at regular interval of time in the range of 1 hr-24 hrs, and respective results are presented in Fig.2. It can be seen that the increase of time, sorption of the metal Cu (II) ions increases to a maximum amount after 24 hrs and the sorption equilibrium reached after the maximum quantity of sorption.

Effect of interference:

Cu (II) was selectively extracted from other transition elements under optimum sorption conditions in binary mixture (Table 1), The separation factor was calculated as the ratio of the distribution ratio (D=[M]org : [M]aq) of Cu (II) to that of the foreign metal ions (K= DCu : DM). In all these separations copper (II) was preferentially sorbed leaving other transition elements in the aqueous phase and thus very high separation factors were achieved. As Cr (III) & Zn (II) interferes to some extent during the extraction of Cu (II), the separation was achieved by masking these ions in aqueous phase using EDTA.

Effect of Temperature:

The Pyridine-2, 6-dimethanol is a hard base due to the presence of 'O' and 'N' donor sites, which preferentially binds hard metal ions Cu (II). Effect of temperature on the sorption of copper by PDM loaded alumina was also monitored and found that optimum temperature. Hence, effect of higher temperature during extraction of Cu (II) is considered, with increase of temperature, absorption of copper increases. It is found maximum sorption at 50^0 C which in Fig.3, and then decreases after the optimum temperature.

Adsorption & Desorption Studies of Cu (II) ions:

The selection of a suitable eluent is one of the important factors to obtain efficiency of the resin and recovery of the metal ion. Low absorption of metal ions at low pH helps to select acidic eluent of hydrochloric acid; nitric acid and thiourea were taken to check the elution studies of Cu (II) ions. Finally, it can be seen, 3mol L-1 of both hydrochloric acid and nitric acid provided high extraction efficiency than other eluants (Table 2). Various volumes of both 3mol L-1 hydrochloric acid and nitric acid were applied for extraction of Cu (II) ion and the extraction efficiency is found to increase by increasing their volume. And quantitative recovery was studied using 5 ml, 10 ml, 15 ml of both 3mol L-1 of HCl and HNO3 for Cu (II) ions.

Analytical Performance:

The pre-concentration factor is one of the most important parameters to evaluate the performance of solid phase extraction method. It was calculated as the ratio of sample volume to the volume of eluants used for quantitative recovery (99.1±1.4%) of Cu (II). The break through volume of sample solution was tested by extracting 0.3175 mg of Cu (II) in 5 ml, 10 ml, and 15 ml of solution under the optimum conditions. The results revealed that the extraction was quantitative in all cases. When 50 ml of sample solution in 3 mol L-1 HNO_3 containing 0.3175 mg of Cu (II) was eluted for certain period of times, it resulted in less than of used solution of Cu (II) in the effluent. Hence preconcentration factor was appreciably high. Precision of the method developed investigated using optimum conditions for adsorption and de-sorption of Cu (II) and expressed in terns of the relative standard deviation (RSD). In six replicate experiments using general procedure, RSD of 1.4% was achieved for Cu (II). The LOD of the proposed method for the determination of Cu (II) was studied under its optimal sorption conditions.

The LOD of the proposed method was appreciable.

The stability and potential reusability of the impregnated sorbent were assessed by monitoring the maximum sorption capacity of Cu (II) through several sorptions-desorption cycles. No significant change was observed, indicating repeated use of the same sorbent may provide an economical route for isolation of Cu (II).

Application:

In order to assess the accuracy and applicability of the proposed method, it was applied to the determination of copper (II) in natural water samples. Synthetic samples were prepared by adding known amounts of copper (II) to the water samples. The results are summarised in (Table 3) and show that, in all cases, the copper recovery is almost satisfactory.

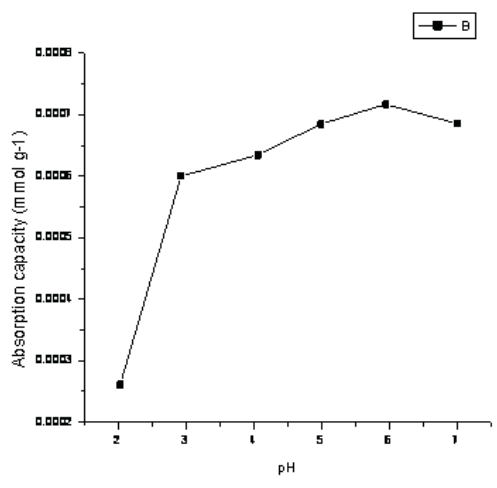

Fig.1: Absorption capacity of the immobilized ligand as a function of pH.

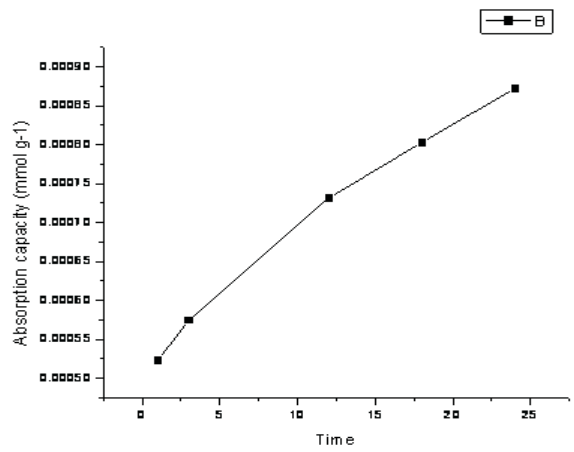

Fig.2: Absorption capacity of the immobolized ligand as a function of time.

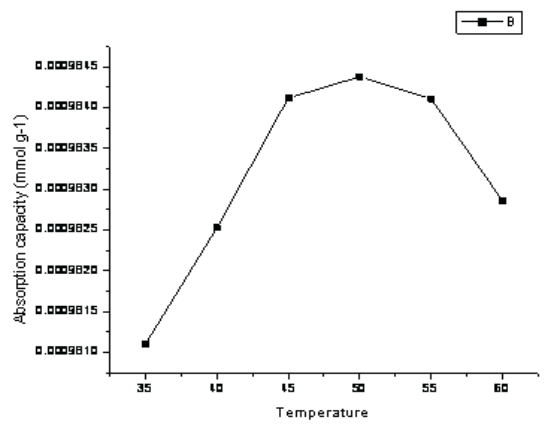

Fig.3: Absorption capacity of the immobilized ligand as a function of temperature.

Table 1: Effect diverse ions on the recovery of Cu (II) from binary mixtures.

Diverse ions	Amount of Cu(II) ion taken in mg(50 ml)	Amount of Cu(II) ion absorbed in m mol g^{-1} by resin	% Recovery	RSD (%)
Cd^{2+}	0.3175	$9.91x10^{-4}$	99.1	2.5
Na^{1+}	0.3175	$9.91x10^{-4}$	99.18	3.5
K^{1+}	0.3175	$9.90x10^{-4}$	99.12	3.2
Ca^{2+}	0.3175	$9.92x10^{-4}$	99.2	3.2
Mg^{2+}	0.3175	$9.90x10^{-4}$	99.13	3.3
Co^{2+}	0.3175	$9.89x10^{-4}$	98.94	1.8
Cr^{3+}	0.3175	$9.66x10^{-4}$	96.9	0.5
Ni^{2+}	0.3175	$9.92x10^{-4}$	99.21	3.8
Zn^{2+}	0.3175	$9.66x10^{-4}$	99.6	0.4
Mn^{2+}	0.3175	$9.92x10^{-4}$	99.21	0.6

Table 2: Effect of different eluants on the % recovery of Cu (II) ion adsorbed on the PDM loaded alumina bed.

Eluants (mol $L^{-1)}$	% Recovery
HNO_3 (1M)	96.8±0.3
HNO_3 (3M)	97.5±1.4
HNO_3 (6M)	94.5±0.4
HCI (1M)	96.5±0.6
HCI (3M)	98.5±1.3
HCI (6M)	95.5±0.8
CH_3COOH (3M)	59.5±1.5
$H_2C_2O_4$	73.2±0.5
Thiourea	49.1±2.0

Table 3: Determination of Copper (II) in the water sample by the proposed method.

Sample	Amount of Cu(II), µg L^{-1}		Recovery (%)
	Added	Found	
Tap water	0.09	0.089	98.88
	5	4.97	99.4
	10	9.98	99.8
Well water	0.08	0.078	97.5
	5	4.95	99
	10	9.02	90.2
Mineral water	0.089	0.083	93.25
	5	5.01	100.2
	10	10.03	100.3
Waste water	0.082	0.08	97.56
	5	5.003	100
	10	10.04	100.4

CONCLUSION:

The proposed spectrophotometric method for Cu (II) ion is simple, sensitive and exihibits good selectivity. The elution of the complex does not involve toxic organic solvents. The method is based upon the preferential sorption of the cationic species of copper (II) prevailing in 1% HNO3 media using pyridine-2,6-dimethanol (PDM) impregnated on alumina. As PDM contains hard donor sites 'O' and 'N' for binding hard metal ion like Copper (II), it was utilized for achieving high enrichment factor for Cu (II). The method showed minimum interferences with commonly found ions in water sample and the recovery of copper (II) was quantitative. The important features of the proposed method are its high adsorption capacity with good pre-concentration factor (>250), a very high reusability for continuous usage (10 cycles), good LOD. The quantitative recovery of copper (II) with a low relative standard deviation of 1.4% reflects the validity and accuracy of the proposed method when applied to real samples. The proposed method was free of interference compared to conventional procedures for determination of copper (II).

REFERENCES:

1.Rahman M. F., M. Phil. Dissertation, Dept. of Chem(BU), India, 2009.
2.O. Samuelson, Ion Exchangers in anal. Chem, John Willey and Sons, New York, 1972, p.4.
3.Moghimi Ali, A J of Basic and Applied Sciences, 6(3) : 349-355, 2012.
4.Hosseini Mehdi & Nasser Dalali, Indian J Chem Tech, Vol.19, sept.2012, pp. 337-341.
5.Hosseini Mehidi, Nasser Dalali, Saeid Md.Nejad, Hosseini et. al.Int.J. of industrial chem 2012, 3:7.
6.Nasser Dalali, Farhangi leila & Hosseini Mehdi, Indian J Chem Tech, Vol.18. May 2011, pp.183-187.
7.Qing Yu, Xiuqing Zhang, Hedong Bian, Hong Liang, Bin Zhao, Shiping Yan and Daizheng Liao, Crystal Growth & Design, 2008. Vol.8.No.4, 1140-1146.
8.Daneshfa A., Ghaedi M., Vafafard S., Shiri L., Sahrai R., Soylak M., Biol Trace Elem Res (2012) 145: 240-247.
9.Ashok Kumar, Pratibha Sharma, Lal Kumar Chandel, Bhagwan Lal Kalal, Sandor Kunsagi-Mate, J Incl phenom Macrocycl Chem (2008) 62:285-292.
10.Anupama Goswami, Ajai K. Singh, Anal Bioanal Chem (2002) 374:554-560.
11.B C Mondal, D Das, A K Das, Talanta 56 (2002) 145-152.
12.Arabinda Kumar Das, Journal of Applied Geochemistry, Vol.4 No.2 (2002) pp 241-253.
13.Özcan YALQINKAY, Orhan Murat KALFA, Ali Rehber TÜRKER, Turk J Chem 34 (2010), 207-217.
14.A.A. Massaoud, H.A. Hanafi, T. Siyam, Z.A. Saleh, F.A. Ali, Cent. Eur.J. Chem.8(1) 2008, 39-45.
15.H. Tavallali, S. Kiani, International Journal of ChemTech Research, Vol.4,No.3, pp 1182-1186.
16.KALLURU VIJAYA KUMAR REDDY, R. KISHORE KUMAR and P. VENKATESHWARLU, Chem Sci Trans, 2013, 2(1), 213-221.
17.Qiufen Hu, Guangyu Yang, Zhangjie Huang and Jiayuan Yin, Bull, Korean. Chem. Soc. 2004, Vol.25, No.4, 545.
18.B. Natesh Kumar, S. Venkateshwarlu, S. Kanchi, N.V.V Jyothi, International Journal of Analytical and Bioanalytical Chemistry, 2013; 3(4): 178-182.
19.Selin Gollu Ozcan, Nuray Satiroglu, Mustafa Soylak, Food and Chemical Toxicology, 48 (2010) 2410-2406.
20.Didarul A. Chowdhury, Md. Ikram ul Hoque, Zeenath Fardous, Jordan Journal of Chemistry, Vol.8, No.2, 2013, pp. 90-102.
21.K Chalapathi, L. Ramesh Babu, V. Rabi and G.P. Maddaiah, Research Journal of Pharmaceutical, Biological and Chemical Sciences, Vol.1, No.3 (2010) pp. 515-523.
22.M. Ghaedi, A. Shokrollahi, A.H. Kianfar, A.S. Mirsadeghi, A. Pourfarokhi, M. Soylak. Journal of Hazadous Materials 2008, 154:128-134.
23.Fazhi Xie, Xucong Lin Xiaoging Wu Zenghong, Xie, Talanta 2008, 74:836-843.
24.Ali Moghimi and Shahriare Ghammamy, Middle-East J.Sci.Res, 12(10): 1331-1338,2012.
25.N. Pourreza, M.R. Fathi and Z. Ardan, J. Iran. Chem. Soc. Vol.7, No.4, Dec.2010, pp.965-971.