DETERMINATION OF CU(II), CO(II), MN(II) AND CD(II) IONS AT TRACE LEVELS BY FAAS AFTER PRECONCENTRATION USING MODIFIED ALUMINA-POLYETHYLENE GLYCOL

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ABSTRACT

In this paper a novel solid phase extraction method to determine Cu (II), Co (II), Mn (II) and Cd (II) using Alumina–Polyethylene Glycol (PEG) as a new adsorbent is described. The method is based on the adsorption of copper, cobalt, manganese and cadmium ions in alkaline media on polyethylene glycol–alumina in a batch method, elution with mineral acid (hydrochloric acid) and determination by Flame Atomic Absorption Spectrometry (FAAS). The adsorption conditions such as effect of pH, amount of adsorbent, preconcentration time, elution time, aqueous phase volume and metal ion concentration were optimized in order to achieve highest sensitivity. The calibration graph was linear in the range of 2.0–100.0 ngmL−1 for Cu (II), 0.5–200.0 ngmL−1 for Co (II), 0.5-300 ngmL−1 for Mn (II) and 1-300 ngmL−1 for Cd (II) in the initial solution. The method was applied to determine Cu (II), Co (II), Mn (II) and Cd (II) in sea water, river water, tap water, metal alloy and grape juice samples.

KEY WORDS

Poly ethylene glycol modified Alumina, FAAS, seawater and grape juice

INTRODUCTION:

Trace metals are widely spread in environment and may enter the food chain from the environment. Some trace metals are essential elements and play an important role in human metabolism. On the other hand, at higher concentrations all metals are recognized as potentially toxic [1]. Therefore, determination of trace heavy metals in different environmental samples is of great interest to analytical chemists. Flame atomic absorption spectrometry (FAAS) is one of the most widely used instruments for determination of heavy metals at trace levels due to its simplicity and lower cost than other instruments. However, there are some limitations in direct determination of heavy metals in environmental samples by FAAS because of matrix interferences and insufficient sensitivity of instrument [2]. Therefore, an initial preconcentration procedure is often required prior to determination of trace metal ions by FAAS. Many preconcentration techniques such as ion-exchange [3], coprecipitation [4], solvent extraction [5], cloud point extraction [6] and solid phase extraction[7–11] have been reported for determination of heavy metals at trace levels in various environmental samples such as natural waters, soil and food. Solid phase extraction is an attractive separation and preconcentration technique for trace metal ions with advantages such as simplicity, flexibility, and high enrichment factor. Various solid phase materials have been introduced for the preconcentration and separation of heavy metal ions. Various adsorbents, such as octadecyl functional groups bonded on silica gel, C18, glycerol–silica gel, chelating adsorbents, Amberlite XAD resins,

Chromosorb resins and other sorbents have been used for adsorption of metal chelates in the preconcentration and separation of metal ions. These include chemically modified silica gel with aminothioamido anthraquinone, polyurethane foam functionalized with naphthol[12], cellulose functionalized with 8-hydroxyquinoline[13], zeolite[14], Amberlite XAD.4 coated with dithiocarbamates[15], carboxylic acid(COOH) bonded to silica gel[16], 8-hydroxyquinoline anchored to silica gel[17], silica gel modified by 2,4,6-trimorpholino-1,3,5-triazin[18], 4,6-dihydroxy- 2-mercaptopyrimidine (DHMP) loaded on activated carbon[19] and naphthalene loaded with tetraoctyl ammonium bromide[20].

The aim of the present work is to establish a new solid phase extraction method for determining Cu (II), Co (II), Mn (II) and Cd(II) at trace levels in environmental, food and metal alloy samples prior to their flame atomic absorption spectrometric determinations. The method is based on the retention of Cu (II), Co (II), Cd (II) and Cd(II) by alumina–polyethylene glycol in a batch method, elution by hydrochloric acid solution and measurement by FAAS.

MATERIALS AND METHODS:

A Varian Spectra GBC 902 flame atomic absorption spectrometer (Australia) equipped with copper, cobalt, manganese and cadmium hollow cathode lamps and air-acetylene flame was used for the analysis. All instrumental settings were those recommended by the manufacturer. The selected wavelengths for determination of copper, cobalt, manganese and cadmium were 324.8nm, 240.7nm, 279.5nm and 228.8nm respectively. Lamp current of 15mA was used for all copper, cobalt, manganese and cadmium. The spectral band pass was 0.1nm, 0.2nm, 0.3nm and 0.4 nm for copper, cobalt, manganese and cadmium respectively. A deuterium back ground correction was also used for copper, cobalt, manganese and cadmium. Slit width, 0.5 nm for all metals, the acetylene flow was 1.5 L min-1 for all metals. FT-IR spectra were recorded on a Bomem FT-IR spectrophotometer (Canada). UV model T90/T90+ PG instruments UV-Visible spectrophotometer (London), TGA –DTA model EXSTAR 6000 (JAPAN), A digital pH-Meter model 632 cyber scan (Japan), with a combined glass electrode was used for pH adjustments was used for analysis.

Analytical reagent-grade chemicals and doubled distilled water were used throughout the study. a stock solution of 1000_gmL−1 of Cu (II) was prepared by dissolving 0.314 g of $(CH_3COO)_2Cu.2H_2O$(Merck) in water and diluting to 100mL in a volumetric flask. A stock solution of 1000_gmL−1 of Co (II) was prepared by dissolving 0.423g of $(CH_3COO)_2$ Co.2H2O (Merck) in water and diluting to 100mL in a volumetric flask. A stock solution of 1000_gmL−1 of Mn (II) was prepared by dissolving 0.307 g of $(CH_3COO)_2Mn.H_2O$ (Merck) in water and diluting to 100mL in a volumetric flask. A stock solution of 1000_gmL−1 of Cd (II) was prepared by dissolving 0.237 g of $(CH_3COO)_2$ Cd.2H2O (Merck) in water and diluting to 100mL in a volumetric flask. The above stock solutions were standardized by EDTA titration [21]. and the working solutions were prepared by appropriate dilution of these stock solutions. A 0.10 mol L−1 solution of NaOH was prepared by dissolving 2.0 g of sodium hydroxide (Merck) in water and diluting to 500mL in a volumetric flask. Neutral Alumina (Aldrich~150 mesh, 50Å and surface area > 200m2/g) was activated by treatment with HCl (5 mol L−1) and dried in vacuum at 120 ∘C. polyethylene glycol (*M*w = 4000), PEG (Merck) was heated at 50 ∘C under vacuum for 40 min before use to remove traces of moisture.

Preparation of sorbent:

Alumina-PEG was prepared by slowly adding 10g of Alumina to a solution of 1g PEG in 25 mL of acetone at 40ºC with constant stirring, after 3hours stirring, the adsorbent was warmed to room temperature by using rotavac evaporator, washed repeatedly two or three times with purified acetone.

The Alumina–PEG adsorbent could be prepared by immobilization of polyethylene glycol on Alumina as previously reported in the literature [22].

Sample preparations:

Sea (collected from the shore of the coast at Chennai), river (Cauvery, Trichy) and tap (NITT) water samples were filtered through a Whatmann filter paper of 40Å pore size. And pH range adjusted with 5mL of hydrochloric acid and sodium hydroxide, stored in polyethylene bottles, kept in the refrigerator before use and filtered prior to analytical procedure. 0.05g of dry metal alloy (Alumina Copper) sample the composition of 95:5%, was weighed into 100mL beaker, 10mL of 1:1 (v/v) hydrochloric acid solution was added and gently stirred for 3 hrs. After cooling at room temperature, the filtrate was dissolved in water and the pH of the final digest was adjusted by the addition of 10% (w/v) sodium hydroxide solution. This solution was finally transferred

to a 250mLvolumetric flask and was subjected to the general procedure. Samples were analyzed with and without addition of metal ions to perform a recovery test

Reaction conditions for real sample analysis:

The reaction conditions were investigated with 4.0 µg Copper, Cobalt, Manganese and Cadmium ions, individually. Adsorption was carried out at different values of pH, while keeping the other variables constant. It was found that Copper, Cobalt, Manganese and cadmium were quantitatively adsorbed on Alumina-PEG in the pH range 8. The pH curves are shown in Fig. 1. In subsequent studies, the pH was maintained at approximately 7-8. The followed preconcentration time

is 3 hours, and the elution time is 30 minutes for all metals Copper, Cobalt, Manganese and Cadmium ions.

Preconcentration by the Preparation of Polymer Metal Adsorption:

0.4g of dry sorbent (Al-PEG) was gently shaken for three hours with 100ml of 10ppm solution of each metal ion at an appropriate pH value. The concentration of metal ions was then determined in the filtrate by FAAS.

Elution of a Metal:

The adsorbed metal ions were eluted with 3.0mLof 2.0 mol L−1of hydrochloric acid and the concentration of each element in the eluent was determined by FAAS separately. A blank solution was also run under the same analytical condition without adding any metal ion.

Table 1: *Comparison of the proposed method with some of the methods reported in the literature.*

System	Preconcentration factor	LOD (ngmL−1)		Ref.
		Ni	Co	
Modified silica gel with aminothioamido anthraquinone	50.0	2.90	0.95	[2]
Cloud point extraction	-	1.10	0.90	[6]
Activated carbon modified by dithioxamide	330.0	0.75	0.80	[8]
Cellulose functionalized with 8-hydroxyquinoline	90.0	1.61	1.09	[12]
Carboxylic acid (COOH) bonded to silica gel	-	2.10	3.10	[15]
8-Hydroxyquinoline anchored to silica gel	200.0	7.50	6.00	[17]
Modified silica gel by 2,4,6-trimorpholino-1,3,5-triazin	100.0	0.29	0.20	[18]
Activated carbon loaded by 4,6-dihydroxy-2-mercaptopyrimidine	260.0	3.50	3.40	[19]
Silica–PEG	83.3	0.71	0.37	[31]

Determination of metals:

Metal in the synthetic solution was thus preconcentrated by solid phase extraction method using the polyethylene glycol modified Alumina as the solid sorbent. All the preconcentration processes were carried out batch wise. The preconcentrated sample of copper, cobalt, manganese and cadmium solutions could be tested in many ways like FAAS, ICP-MS; ICP-AES. In this work, the eluate collected after the elution was analyzed with Flame Atomic Absorption Spectrophotometer (FAAS). The AAS instrument used for the metal ion determination was GBC902.

Recommended procedure for simultaneous preconcentration:

A 100mL RB flask with a very cleaned one was packed with 0.4 g of the Alumina–PEG adsorbent and used for simultaneous preconcentration of Cu (II), Co (II), Mn (II) and Cd(II). 100mL of the solution containing 25mL of 10ppm Copper (II), Cobalt (II), Manganese (II) and

Cadmium (II) solutions, NaOH and HCl was used for adjusting pH value. The adsorbed metal ions were eluted with 3.0mL of 2.0mol L−1of HCL and the concentration of each element in the eluent was determined by FAAS separately. A blank solution was also run under the same analytical conditions without adding any Cu (II), Cu (II), Mn(II) and Cd(II).

RESULTS

Alumina-grafted polyethylene glycol has been successfully applied as a solid–liquid phase-transfer catalyst by organic chemists. It seems that this polymeric catalyst could form complexes with cations much like crown ethers [22]. Therefore, polyethylene glycol was easily immobilized on Alumina and used as a new adsorbent for preconcentration of copper, cobalt, manganese and cadmium ions. In order to improve the recovery of preconcentration, the effect of various variables was studied and optimized. The percent of

metal ions adsorbed on the adsorbent was calculated from the amounts of metal ions in the starting sample and the amounts of metal ions eluted from the adsorbent.

Adsorbent characterization:

The PEG-grafted alumina particles are special type of branched inorganic–organic copolymer which has polyether functional groups in the side chains that has been found to be stable to acid, base, high temperature and oxygen. Its FT-IR spectrum shows the presence of OH and ethylene oxide groups on the surface of the adsorbent.

Optimization studies for extraction of metal:

Several analytical parameters were optimized for effective preconcentration of copper, cobalt, manganese and cadmium from real samples.

Effect of pH on metal ion uptake properties:

The pH is a very important parameter for the metal uptake of the adsorbing agents on solid polymeric material (sorbent). The adsorption of metal ions was performed in both acidic and alkaline media. The preliminary investigation showed that the metal ions are retained by the adsorbent in the alkaline solution. The decrease of pH leads to neutralization of surface charge; thus, the adsorption of cations should decrease [23]. Ionization of the adsorbing adsorbent and the stability of the metal-adsorbent adsorption vary, when changing the pH. In general, the metal uptake was seen to increase significantly with increasing pH up to a pH of 8 and then it started to decrease after 8. The adsorbed stability depended strongly on the pH, as the affinity and stability of the adsorption increased. The result indicated the Copper, cobalt, manganese and cadmium was adsorbed selectively the higher extend over the pH range**.**
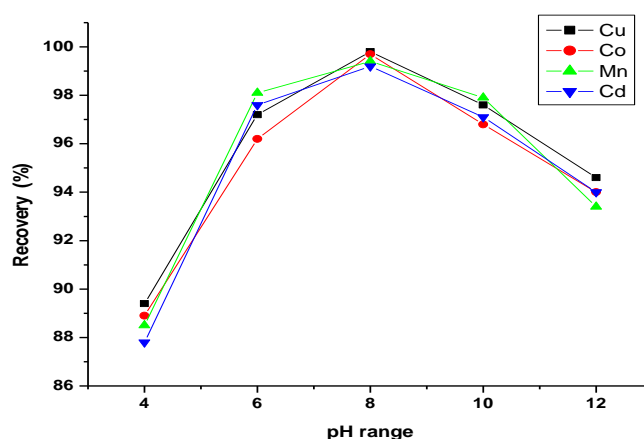

Fig.1. Effect of pH on the recovery of 10 ngmL−1 Cu (II), Co (II), Mn (II) and Cd(II).

As presented in Fig. 1 the highest recoveries are obtained for all metal ions at pH 8. Therefore, pH of 8 was selected for further investigations.

Effect of the weight:

The amount of solid phase material is another important factor on the batch studies for quantitative recovery. In order to estimate the optimum adsorbent quantity, the recoveries of Cu(II), Co(II), Mn(II) and Cd(II) were examined by using the adsorbent quantities in the range of 0.1–0.5 g. The results shown in Fig. 2 indicate that quantitative recoveries were achieved when adsorbent quantity was greater than 0.1 g. In the proposed procedure, 0.4 g of the adsorbent was used in further experiments. The amount of adsorbent increases the metal uptake also increase but it reached some certain amount the uptake capacity of the adsorbent saturated. The maximum metal uptake was obtained at 0.4g. Containing 0.4 g of adsorbent can be used three times without any loss in the recovery. The used adsorbents can also be recovered by a simple procedure. Used Alumina–PEG was stirred with 100mL of 5% hydrochloric acid for 2 h, filtered and dried. The recycled adsorbent can be used three times again, thus the consumption of the adsorbent is too low because it can be recycled several times without any loss in the sensitivity.
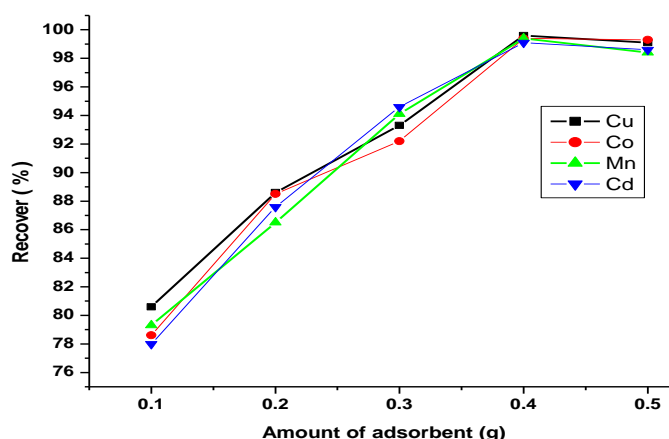
Fig. 2. Effect of weight on the recovery of 10 ngmL−1 Cu (II), Co(II), Mn(II) and Cd(II)

As presented in Fig. 2 the highest recoveries are obtained for all metal ions at 0.4(g). Therefore, 0.4(g) was selected for further investigations.

Effect of preconcentration time:

Preconcentration time was the time allowed for the adsorbent to be in contact with metal ion solution. Both the stirring and digestion processes were included in the preconcentration time. The saturation time for the metal uptake of the adsorbent was obtained by plotting percentage metal uptake against contact time, keeping the initial metal ion concentration constant. The minimum time needed for good enrichment of copper, cobalt, manganese and cadmium was 3 hours.
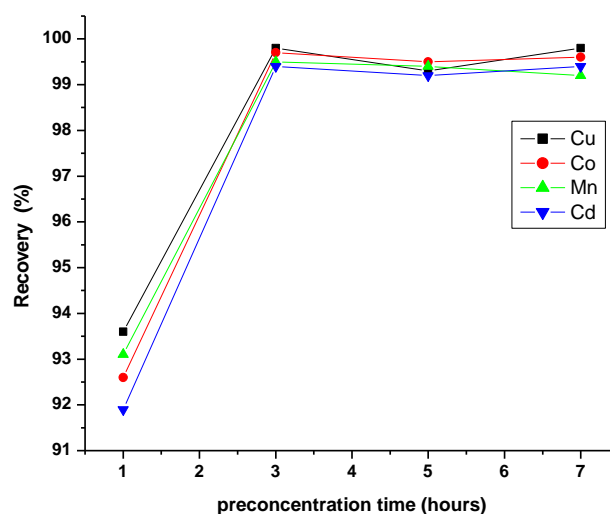

Fig. 3. Effect of preconcentration time on the recovery of 10 ngmL−1 Cu(II), Co(II), Mn(II) and Cd(II).

As presented in Fig. 3 the highest recoveries are obtained for all metal ions at 3 hrs. Therefore, 3hrs was selected for further investigations.

Effect of elution time parameter:

The minimum time required to carry out elution of the metal from the sorbent is called elution time. The maximum extraction was 40 minutes. A satisfactory eluent should effectively elute the adsorbed metal ions with small volume in order to achieve high enrichment factor. Various acids and organic solvents such as acetone, hexane, ethanol, HCl and HNO3 were tested as the eluent for desorbing metal ions from the adsorbent surface. Among the solvents studied, hydrochloric acid provided higher recovery compared to other solvents. Therefore, the effect of hydrochloric acid concentration was studied. As the results in Fig. 4 show, the highest recoveries were obtained when 0.10–0.25 mol L−1 of hydrochloric acid was used as an eluent. The effect of the volume of the eluent was also studied and 3.0mL of 0.2 mol L−1 of hydrochloric acid was selected as the

optimum value because it was sufficient for quantitative recovery of the metal ions.
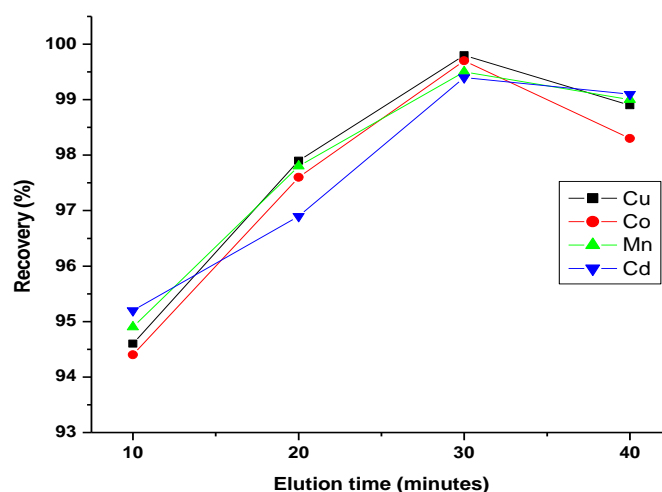

Fig. 4. Effect of elution time on the recovery of 10 ngmL−1 Cu(II), Co(II), Mn(II) and Cd(II).

Effect of metal ion concentration:

The impact of metal ion concentration on the extraction procedure was studied. When the concentration of metal ion increased, the enrichment efficiency increased, but it reached some certain amount the uptake capacity of the adsorbent saturated and starts decreased. i.e., when the amount of metal ions was high in a particular volume of water, the separation of the metal increased.
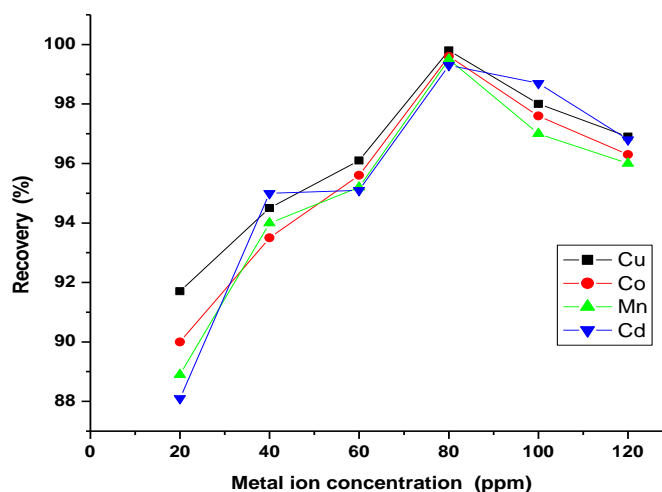

Fig. 5. Effect of metal ion concentration on the recovery of 10 ngmL−1 Cu (II), Co (II), Mn (II) and Cd (II).

As presented in Fig. 2 the highest recoveries are obtained for all metal ions at 80ppm. Therefore, 80ppm was selected for further investigations.

Effect of Aqueous Phase Volume:

Solutions containing 0.314 g of copper were diluted from 50 to 500mL by deionized water and copper, cobalt, manganese and cadmium was analyzed by the general procedure. The effect of aqueous volume in batch method was studied with 0.4 g of adsorbent equilibrated at optimum pH for 5 hours. It was observed that the adsorption of copper, cobalt, manganese and cadmium remained constant up to 500ml. The volume of aqueous phase is an important factor for the adsorption of metals. They indicated that the exchange reaction of copper, cobalt, manganese and cadmium was rapid and the efficiency was high.
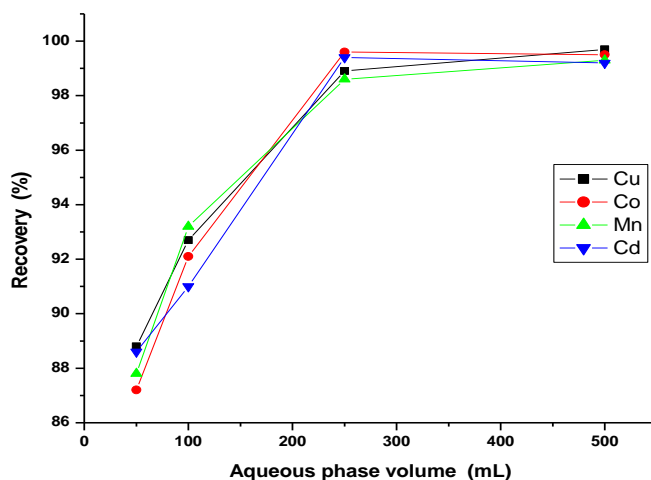
Fig. 6. Effect of aqueous phase volume on the recovery of 10 ngmL−1 Cu (II), Co (II), Mn (II) and Cd (II).

As presented in Fig. 6 the highest recoveries are obtained for all metal ions at 500(mL). Therefore, 500(mL) was selected for further investigations.

Interference studies:

In order to examine the effect of different ions on determination of Cu (II), Co (II), Mn (II) and Cd (II), constant amounts of Cu (II), Co(II), Mn(II) and Cd(II) were taken with different amounts of ions and subsequently the general procedure was followed. Any deviation of ±5% or more from the absorbance value of the standard solution was considered as interference. The results presented in Table 1 show that a large number of ions tested have no effect on determining Cu (II), Co (II), Mn (II) and Cd (II).

The effect of interfering ions in real samples concentrate such as NaCl, NaNO$_3$, Na$_2$SO$_4$, KCl, MgCl$_2$, CaCl$_2$ on solid phase extraction were studied. Interfering ions are separately added to the solution containing metals and the present procedure was followed. The matrices contents in the eluent solution were found to be significantly lower and suitable for FAAS determination.

Recommended procedure for simultaneous preconcentration:

A 100mL RB flask with a very cleaned one was packed with 0.5 g of the Alumina–PEG adsorbent and used for simultaneous preconcentration of Cu (II), Co (II), Mn (II) and Cd (II). 100mL of the solution containing 25mL of 10ppm Copper (II), Cobalt (II), Manganese (II) and Cadmium (II) solutions of NaOH was used for adjusting pH value. The adsorbed metal ions were eluted with 3.0mL of 2.0mol L−1of HCL and the concentration of each element in the eluent was determined by FAAS separately. A blank solution was also run under the same analytical conditions without adding any Cu (II), Cu (II), Mn (II) and Cd (II). Above table indicates that the priority of metal adsorption series is Cu (II) > Co (II) > Mn (II) > Cd (II).

Table 2: *Effect of interference ions for sea water*

Sl.No.	Composition of Interfering ions (g)	Metals	% uptaken
1.	NaCl (0.5), NaNO$_3$ (0.5), Na$_2$SO$_4$ (0.5),KCL(0.5), MgCl$_2$(0.5), Cacl$_2$ (0.5)	Cu	95.1%
		Mn	92.2%
		Co	90.3%
		Cd	86.6%

FT IR spectra of the synthesized Al-PEG and metal adsorbed Al-PEG:

Infrared spectrum of alumina modified polyethylene glycol and Al-PEG-Cu was recorded in KBr medium (400-4000cm^{-1}) exhibited a number of bands as shown in above spectrum. The tentative assignments of various streching and bending frequencies in comparison with IR absoption bands of alumina modified polyethylene glycol and Al-PEG-Cu listesd in table.4. Alumina modified polyethylene glycol shows number of

absorption bands and the absorption frequencies are in a slightly shifted position compared with those of the reactants, alumina modified polyethylene glycol and Al-PEG-Metal adsorption. The peak observed at 3416 cm^{-1} may be assigned to the –OH group. The peak observed 2877.58 cm^{-1} indicates the - CH$_2$O (sym) and the peak 1116.91 cm^{-1} may be attributed bending vibrations of - OH group. The absorption band at 1417 cm^{-1} indicates the -OH inside the plane. In 3.3µµ.2. IR spectra of Al-PEG-Cu spectrum displays the absence of some peaks. The peaks absence at 1116.91 cm^{-1} ,2877.58 cm^{-1} may be assigned due to the formation of Al- PEG-Metal adsorption

Table 3: *Results for simultaneous preconcentration*

Sample	Metal	Absorbance		Recovery (%)
		Stock (ngmL−1)	Found (ngmL−1)	
Each 25mL of Cu (II)+ Co (II)+ Mn(II)+Cd(II) solution	Cu	0.456±0.5	0.469	98
	Co	0.126±0.2	0.070	60
	Mn	0.092±0.4	0.033	40
	Cd	0.069±0.1	0	0

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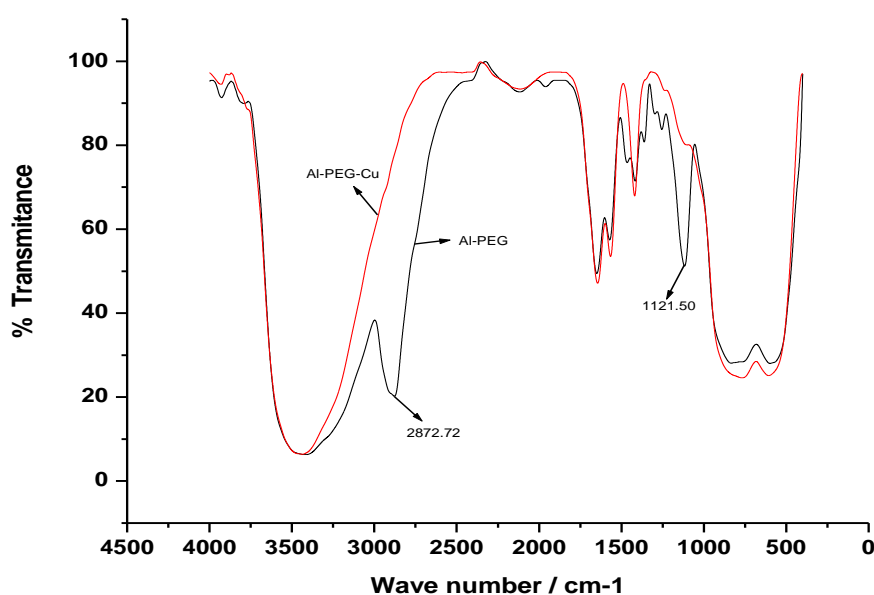

Fig. 7. FT IR spectra of the Al-PEG and metal adsorbed Al-PE

The structurally important absorption frequencies of adsorbent and metal adsorption have been presented in the above UV spectra result. The ligand band at 527.2(nm) indicating the of adsorption PEG to the metal atom.
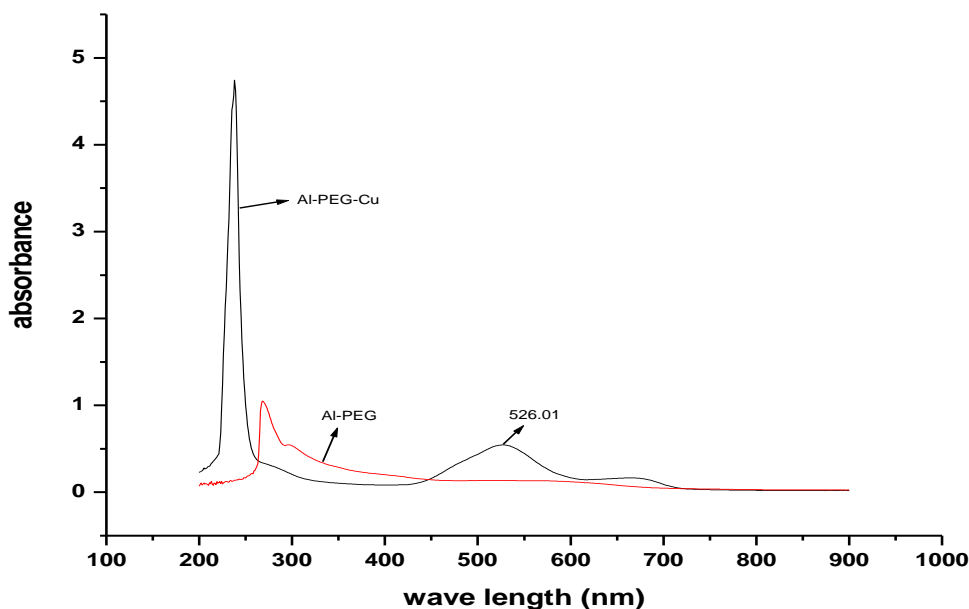
UV- data for Al-PEG-Cu, PEG:

Fig. 8 uv visible data for the synthesized Al-PEG and Al-PEG-Cu
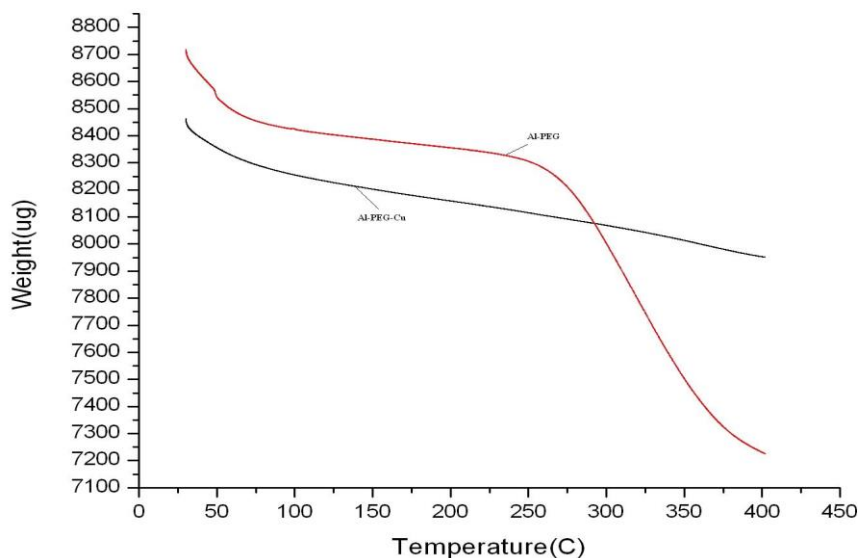

Fig.9. TGA results for the synthesized Al-PEG and Al-PEG-Cu (weight loss in µg)

Table 5: *TGA results for the synthesized Al-PEG and Al-PEG-Cu (% of weight loss)*

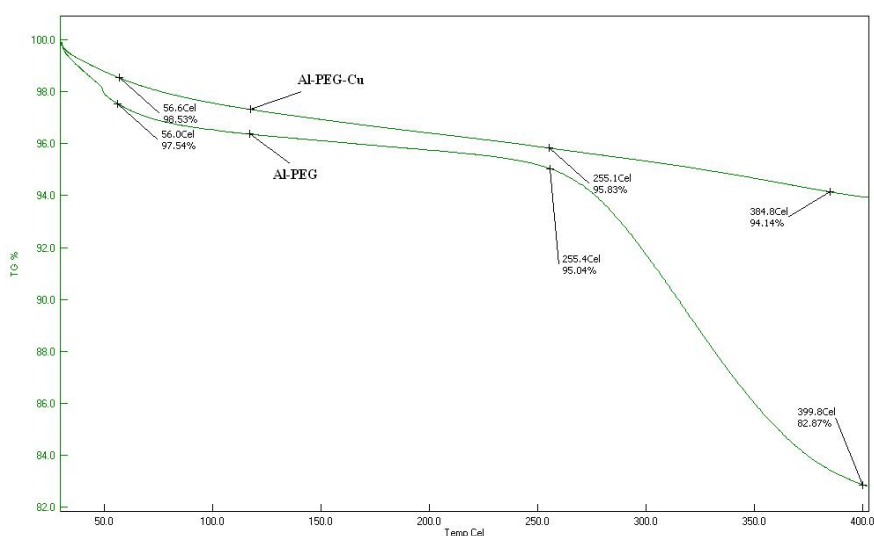| S.No.	Temperature (°C)	% of weight loss	
		Al-PEG (%)	Al-PEG metal complex (%)
1.	56	2.46	1.47
2.	255	4.96	4.17
3.	400	17.13	5.86

Fig.10. TGA results for the synthesized Al-PEG and Al-PEG-Cu (weight loss in %)

The above result indicates that, Al-PEG metal complex is more stable than Al-PEG

Table 6: *Determination of Mn (II) in Grape juice samples*

Sample	Metal	Added Concentration (ngmL−1)	Found (ngmL⁻¹)	Recovery (%)
Grape juice	Mn	-	1.6 ± 0.2	-
		10	11.6 ± 0.6	100
		20	20.7 ± 0.1	101

Sorbent Regeneration:

To be viable material for sorbent system they must be chemically stable. The sorbent could be easily regenerated with 1:1 HCl. To obtain sorbent reusability, the sorption- desorption cycle was repeated four times with the same adsorbent. More than 95% of the desorbed metal ions were removed using 1:1 HCl. This revealed the good recyclability and stability of the adsorbent under acidic condition.

Table 7: *Determination of Cu (II), Co (II), Mn (II) and Cd (II) in Sea water sample*

Sample	Metal	Added Concentration (ngmL−1)	Found (ngmL−1)	Recovery (%)
		-	6.5 ± 0.2	-
	Cu	10	16.5 ± 0.5	100
		20	26.7 ± 0.3	102
		-	4.6 ± 0.3	-
	Co	10	14.6 ± 0.2	100
		20	24.7 ± 0.6	101
Sea water		-	1.2 ± 0.1	-
	Mn	10	11.1 ± 0.6	99
		20	21.3 ± 0.2	101
		-	2.6 ± 0.1	-
	Cd	10	12.5 ± 0.3	99
		20	22.8 ± 0.5	102

Table 8: *Determination of Cu (II), Co (II), Mn (II) and Cd (II) in River water sample*

Sample	Metal	Added Concentration (ngmL−1)	Found (ngmL−1)	Recovery (%)
River water	Cu	-	4.61 ± 0.4	-
		10	14.5 ± 0.5	99
		20	24.87 ± 0.3	102
	Co	-	3.0 ± 0.3	-
		10	13.0 ± 0.2	100
		20	23.2 ± 0.6	102
	Mn	-	2.2 ± 0.3	-
		10	12.1 ± 0.6	99
		20	22.3 ± 0.2	101
	Cd	-	1.1 ± 0.1	-
		10	11.1 ± 0.6	100
		20	21.3 ± 0.4	102

Table 9: *Determination of Cu (II), Co (II), Mn (II) and Cd (II) in Tap water sample*

Sample	Metal	Added Concentration (ngmL−1)	Found (ngmL−1)	Recovery (%)
Tap water	Cu	-	2.5 ± 0.4	-
		10	12.5 ± 0.5	99
		20	23.77 ± 0.3	102
	Co	-	3.3 ± 0.3	-
		10	13.3 ± 0.6	100
		20	23.4 ± 0.6	101
	Mn	-	2.1 ± 0.1	-
		10	12.1 ± 0.5	100
		20	22.2 ± 0.3	101
	Cd	-	0.6 ± 0.1	-
		10	10.6 ± 0.5	100
		20	20.8 ± 0.3	102

Table 10: *Determination of Cu (II) in Alloy samples*

Sample	Metal	Added Concentration (ppm)	Found (ngmL−1)	Recovery (%)
Metal alloy	Cu	0	12.6 ± 0.5	-
		10	22.6 ± 0.3	100
		20	32.9 ± 0.2	103

Application:

The proposed solid phase extraction procedure was applied to determine copper, cobalt, and manganese and cadmium ions in sea water, river water, tap water, metal alloy and grape juice samples. The results are given in Tables 6, 7, 8, 9 and 10. Different amounts of the investigated metal ions were also spiked to the samples and the resulting solutions were submitted to the preconcentration procedure. Good agreement was achieved between the added and found concentrations of analytes using the recommended procedure. The recovery values for the analyte ions were in the range of 99–103%. In order to estimate the accuracy of the procedure, these values revealed that there is good agreement between the two methods and there was also no significant difference between the results by performing t-test at 95% confidence limit.

CONCLUSION

In this paper we showed the analytical performance of Alumina modified PEG for preconcentration of trace amounts of copper, cobalt, manganese and cadmium in sea, river, tap water, grape juice and metal alloy Samples and simultaneous determination. Alumina modified PEG represents a potentially significant advancement in the field of preconcentration and

analytical separation due to its high surface area, thus making possible the free interference preconcentration of copper, cobalt, manganese and cadmium ions in different matrices. The performance of proposed method was significantly better than that of previous method with respect to preconcentration system, including satisfactory preconcentration factor and preconcentration efficiency, and thus resulting in a lower limit of detection. Moreover, the prepared adsorbent is eco-friendly and very economical because it can be recycled and used several times without any loss in the recovery and it was shown that the method is characterized by simplicity, precision and the absence of organic solvent used as eluent. The method is highly sensitive and selective for determination of trace amounts of Cu (II), Co (II), Mn (II) and Cd (II) by flame atomic absorption spectrometry.

To the best of our knowledge, this is the first application of Silica–PEG as an adsorbent for preconcentration of metal ions.

The sorbent finds broad applications as preconcentrations and separation matrix for metal ion. It exhibits good characteristics for adsorption and preconcentration of Cu (II), Co (II), Mn (II) and Cd (II) in aqueous solution. It has a superior reusability and stability, the investigated adsorbent has been studied for the quantitative separation of Cu (II), Co (II), Mn (II) and Cd (II) and it can be applied to any other transition metals.

The detection limits for copper, cobalt, manganese and cadmium ions are better than or comparable to some of the previously reported values. A comparison with some of the previous works is also given in Table 1. The method was successfully applied to the determination of Co (II) and Ni (II) in black tea, sesame seeds, rice flour, tap water and river water samples.

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