Original Research Paper

Determination of Mercury and Manganese by Using New Reagent Azo after Cloud Point Extraction for Some Environmental Sample in Iraq

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Abstract: A new reagent of Azo was papered for determination of Hg^{+2} and Mn^{+2} by Cloud Point Extraction (CPE) method. Procedure which was developed for the separation and preconcentration and the procedure are simple, cheap, fast and environmental safety. The parameters affecting could point extraction, such as concentrations of reagent, volume of triton X-100, pH, equilibrium of temperature and time-consuming were studded. Under the optimum condition the linear range 2-14 μg L^{-1} for mercury and 2-16 μg L^{-1} for manganese at pH 7. The detection limit was 0.75, 0.4 μg L^{-1} and relative standard deviation was 1.3%, 1.4% respectively, the recovery of analytes was found 96-98.7%, 97-99.7%. The method was applied to the determination of manganese (II) and mercury(II) of wastewater of Rustimiyah city in Iraq.

Keyword: Cloud Point Extraction, 3-[(5-Hydroxy-3-6, 6-Trimethylclohexa2,4-Dienyl)Diazenyl]Phenol, Determination Mercury and Manganese

Introduction

Almost all mercury compounds are toxic and can be dangerous at very low levels in both aquatic and terrestrial ecosystems. Because mercury is a persistent substance, it can build up (Li and Hu, 2007). Mercury and mercury compounds are some of the most regulated of all chemicals. The Environmental Protection Agency (EPA) is responsible for regulating discharges of mercury and mercury compounds into the environment (atmosphere, waters and landfills) (Scarmoutzos and Boyd, 2004). Manganese has been called as a rare element; it was found a trace amount in human body more than it is important in biochemistry which plays as co-factor for several enzymes and plays a role in establishing tissue (Velasco-Ryenolda *et al*., 2008), fat and bone. The low concentration of metal ions in sample and the matrix interference which requires sensitive apparatus techniques, pr-concentration, separation such as liquid-liquid extraction (Roundhill *et al*., 2009), solid phase extraction (Yang *et al*., 2004), last decade use cloud point extraction (Manzoori and Bavili-Tabrizi, 2002). Different reagent of azo and Schiff base use to determination ions by (CPE) method such as 1-(2-thiazolylazo)-2-naphthol(TAN)(Chen and Toe, 2001), 2-(5-bromo-2pyridylazo)-5-diethylaminophenol(5-Br-PADAP) (Wuilloud *et al*., 2008), -(2-thiazolylazo)-p-cresol (TAC) (Portugal *et al*., 2007), (2-pyridylazo) resorcinol (PAR) (Doroschuk *et al*., 2004), PMBP (Manzoori and Abodlmohammad-Zadeh, 2007) and Schiff base such as N,N'-bis (salicylidene) ethylenediamin [SALEN] (Bakir and Dhahir, 2013), E-4-(3-hydroxybenylideneamino) 1,5 dimethyl-2-phenyl-1Hpyrazol- 3(2H)-one[4-(HBDA1), 5DPHPO] (Dhahir and RhajabBakir, 2015), Bis((1H-benzo[d]imidazol-2yl) methyl) sulfane[BHIS] (Ahmad *et al*., 2011), N-salicylideneaniline (SA) (Youcef *et al*., 2006).

Instrumentation and Apparatus

Instruments

A thermo stated water bath model Memmert, UV-Visible model HACH, FTIR Shimadzu, model IR-PRESTIGE 21, Japan, PH meter HANNA 211, Phase separation was achieved with centrifuge TG-04S TABLE-TOP of 4100 rpm.

Regents

All the chemicals used were of analytical reagent grade; deionize water use to diluting the samples. Hydrochloric acid (BDH), Triton X-100 (Merck), Sodium hydroxide (BDH), sodium nitrate (BDH), thymol (BDH), ethanol (Merck), manganese sulphate mono hydrate (GCC), 3-amino phenol (BDH). About 1000 μg L^{-1} stock solution of Mn^{+2} and Hg^{+2} were prepared by dissolving 0.1353, 0.159 g of mercury(II) chloride and manganese sulphate mono hydrate an appropriate amount of deionized water and diluting to the mark in 100 mL volumetric flask. Working stock solution was prepared daily from the stock by appropriate dilution with water. Stock solution of HTMCDAP reagent was prepared by dissolving 0.258 g in 0.5 mL of 10%(V/V) TritonX-100 and diluting to the mark in 100 mL. Non-ionic surfactant, TritonX-100 10%(V/V) was prepared by dissolving 10 mL Triton X-100 in hot deionize water and diluting to the mark in 100 mL volumetric flask. 0.01 M hydrochloric acid and 0.01 M sodium hydroxide use to adjust pH.

General Procedure for CPE

Aliquots 10 mL of a solution containing a known amount of Mn^{+2}, Hg^{+2} ions, 10% (v/v), Triton x-100 and reagent was adjusted the pH by 0.01 M HCl, 0.01 M NaOH. The mixture was shaken for 1 min and left to stand in a thermo-stated bath at 70°C for 15 min. Separation of the phases was achieved by centrifugation at 4100 rpm for 15 min the remaining of micelle phase was dissolved by ethanol, Mn^{+2} and Hg^{+2} ions were measured by UV-Vis spectrophotometer at λ_{max} 444 and 423 nm.

Synthesis and Characterization of Reagent

The synthesis of 3-[(5-hydroxy-3-6,6-trimethylclohexa2,4-dienyl)diazenyl]phenol scheme(1) was synthesized according to the reported method by dissolved 3g (0.027 mol) of C6H4(NH2)(OH) in 5 mL of concentrated hydrochloric and 5 mL deionized water and diazotized below 5°C with (0.75 g, 0.01 mol) of sodium nitrite. The resulting diazonium chloride solution was added drop wise with cooling to solution of thymol 4g (0.026 mol) dissolved in 5 mL of alkaline ethanol; the solid product was filtered and crystallized from hot ethanol.

Results and Discussion

The FTIR Spectrum of Ligand HTMCDAP and Complexes

The FTIR spectra of free ligand showed an appearance of broad band's at (1438 cm^{-1}) refer to the frequency of azo group confirmed that a synthesized dye containing azo group (Veerachalee *et al.*, 2007). Table 1 and Fig. 1 showed the broad bands of ligand HTMCDAP in KBR disk.
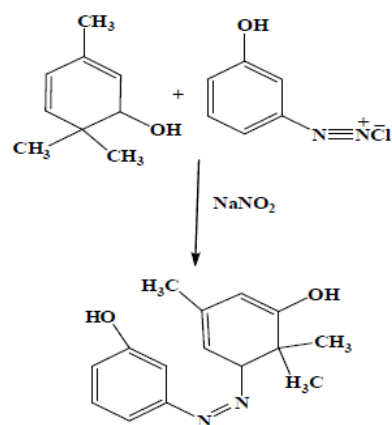
The FTIR spectra of free ligand showed two bands at (3429, 3178 cm^{-1}) refer to the frequency of ν(OH) of phenolic group respectively, while in the metal complexes observed that the disappearing of one band for ν(OH) vibration in the spectra of Hg-HTMCDAP and Mn-HTMCDAP, indicating the coordination of phenolic oxygen with metal ions (Mohammed and Asniza, 2010). The spectra bands of the free ligands at 1438 cm^{-1} refer to azo group ν(N = N) shifting to higher bands in the metals complex's observed at (1458,1454 cm^{-1}). The infrared spectra of the complexes have shown some other new bands which appeared in the range (582-520 cm^{-1}), (594-51 cm^{-1}) and (482-424 cm^{-1}), (466-405 cm^{-1}) are due to the ν(M-O) and ν(M-N), respectively (Al-Bayati *et al.*, 2013; Nakamoto, 1997) for Mn-HTMCDAP and Hg-HTMCDAP. Figure 1 to 3 shown the FTIR for Ligand and complex's.

Ultraviolent Spectrum of Ligand HTMCDAP and Hg-HTMCDAP and Mn- HTMCDAP

The UV-Vis spectrum of HTMCDAP shown maximum absorption at 294 nm due to the ($\pi{\rightarrow}\pi^*$), the azo group (N = N) gives an absorption in the 397 nm (Kirkan and Gup, 2008). The complex with Hg-HTMCDAP and Mn-HTMCDAP the maximum absorption were appeared at 444 and 423 nm while the ligand at 397 nm maximum absorption. Figure 4 to 6 shown the UV/VIS for ligand and complexes.

C.H.N Analysis

The results of element analysis of new reagent HTMCDAP were explain in Table 2.

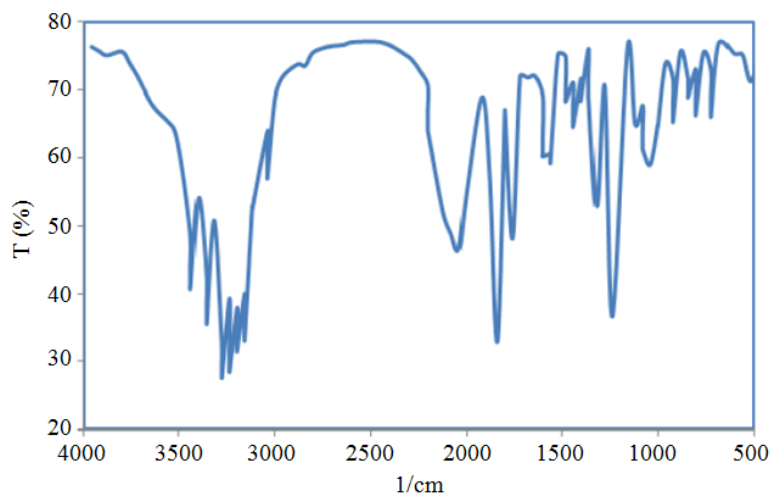Schem 1. The chemical structure of Reagent HTMCDAP
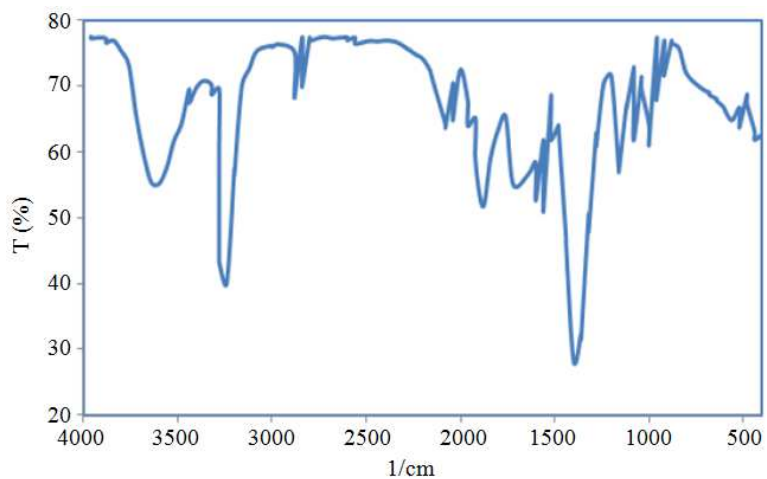
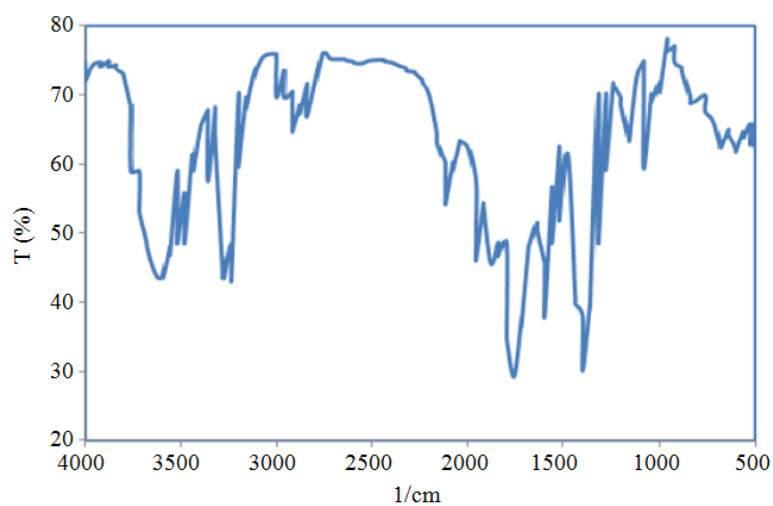Fig. 1. FTIR of ligand HTMCD

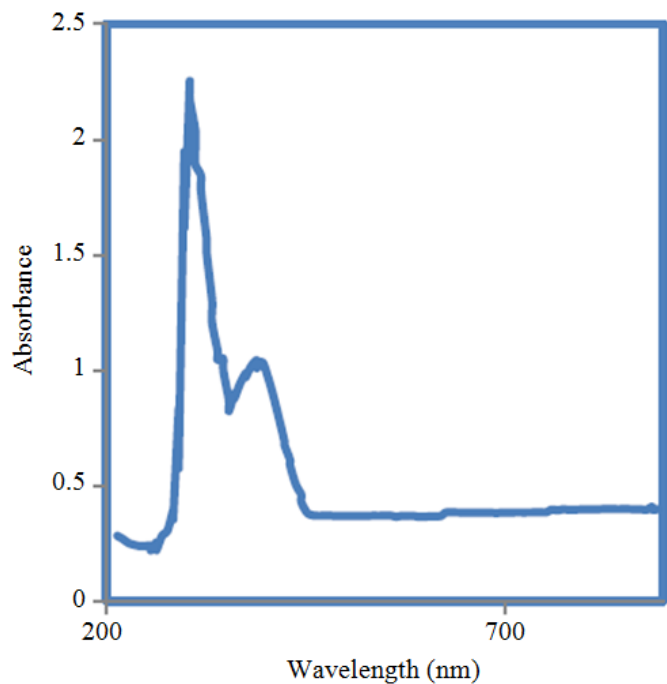Fig. 2. FTIR of Mn-HTMCDAP

Fig. 3. FTIR of Hg-HTMCDAP
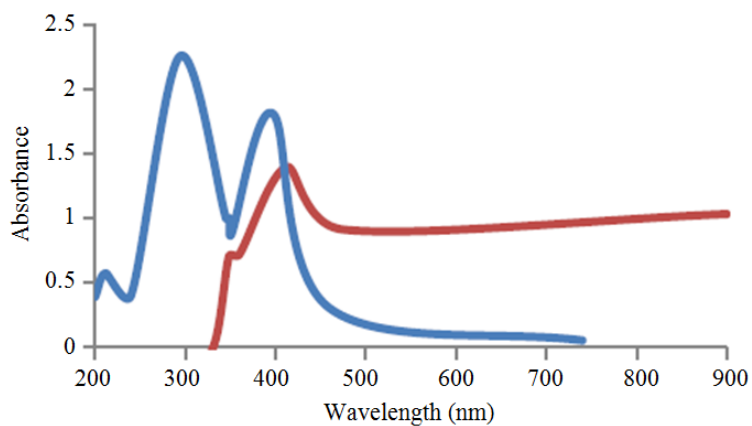
Fig. 4. The spectrum of ligand

Fig. 5. The spectrum of complex Mn-HTMCDAP

Fig. 6. The spectrum of complex Hg-HTMCDAP

Table 1. IR data (400-4000 cm^{-1}) of HTMCDAP

IR bands	Wave number cm^{-1}
O-H stretching	34,293,178
C-H aromatic	3066
C-H aliphatic	29,622,924
N = N	1438
C = C	1381
C-H (s, δ, bend aromatic)	905,883,848

Table 2. Elemental analysis of HTMCDAP by C.H.N

	Percentage				
	C15H18N2O2			258.32	
C	H	N	S		Calculation
69.74	7.02	10.84	0.0		Theoretical
70.76	6.93	11.11	0.0		Practical

Optimization of CPE Procedure

Effect of pH

The pH plays a critical role on metallic complex formation and has been a significant parameter for CPE, the aqueous solutions on the extraction yield of Mn^{+2} and Hg^{+2} as HTMCDAP reagent were investigated in the pH range 4-14, the maximum sensitivity for CPE was obtained at pH 7 the results are shown in Fig. 7. In more acidic solutions due to protonation the reagent while in the basic solution due to formation of charged hydroxyl-M-HTMCDAP mixed complexes or precipitation of metal ions in the form of hydroxides. So as the pH 7 was chosen.

Effect of HTMCDAP Concentration

The concentration of reagent is important indicator as to whether the reagent action processed completely. The effect of HTMCDAP concentration on the absorbance was investigated within range (1×10^{-5}-9×10^{-5}) mol L^{-1}, the results are shown in Fig. 8. Shows that the measured absorbance increases when the concentration of HTMCDAP increases and then suddenly decreased up concentration 7×10^{-5} mol L^{-1}, therefore 7×10^{-5} mol L^{-1} was chosen.

Effect of Triton X-100 Volume

Figure 9 has shown effect of surfactant volume on the cloud point extraction of Mn^{+2} and Hg^{+2}. Different volumes of 10% (v/v) Triton X-100 ranging from (0.1-1) mL, the highest absorbance was found at 0.8 mL of 10% (v/v) Triton X-100 up this TritonX-100 volume, the analytical signal starts to decrease. This can be attributed to an increase in viscosity of the surfactant phase. Thus, 0.8 mL of 10% (v/v) Triton X-100 was used as optimal.

Effect of Equilibrium Temperature and the Incubation Time

The effects of the equilibrium temperature and the incubation time are important factors in (CPE) and efficient separation of phases. Absorbance was investigated in the range of 40-95°C and 5-35 see and the results is shown in Fig. 10 and 11. Excellent absorbance was found at temperature 85°C for Hg^{+2} and 70°C for Mn^{+2} at higher temperature could cause decomposition of the complex. It was also observed the maximum absorbance found at 25 and 30 min for Hg^{+2} and Mn^{+2} thus, selected 25 and 30 min.

Interferences Study

The effect of most diverse ions expected in the wastewater sample of Rustimiyah city in Iraq on the determination of 14 μg L^{-1} Hg^{+2} and 16 μg L^{-1} Mn^{+2} under the optimal condition, cations may react with reagent and anions may form complex's with Hg^{+2} and Mn^{+2} thus, extraction efficiency decreases. Table 3 shown the effect of Interferences ions.

Calibration Graph

Employing the optimum conditions established by CPE procedure to determination Hg^{+2} and Mn^{+2}, the calibration graph response to the Beer law over the concentration 2-14 μg L^{-1} for mercury and 2-16 μg L^{-1} for manganese with correlation coefficient 0.9982, 0.9961 are shown in Fig. 12 and 13. All other analytical characteristics data are summarized in Table 4.

Continuous Variation Method

A series of range from 1 to 9 mL of 7×10^{-5} mol L^{-1} Hg^{+2} and Mn^{+2} was pipetted into each of eleven 10 mL volumetric flask, then 9, 8,7,6,5,4,3,2,1 mL of 7×10^{-5} mol L^{-1} HTMCDAP reagent added into each volumetric

flasks at optimum pH, the absorbance of the solutions were measured by UV-visible spectrophotometer. The stoichiometric ratio between Hg^{+2}- HTMCDAP and Mn^{+2}- HTMCDAP is shown in Fig. 14 and 15. Predict structure for the complex is 1:2 as shown in scheme 2.
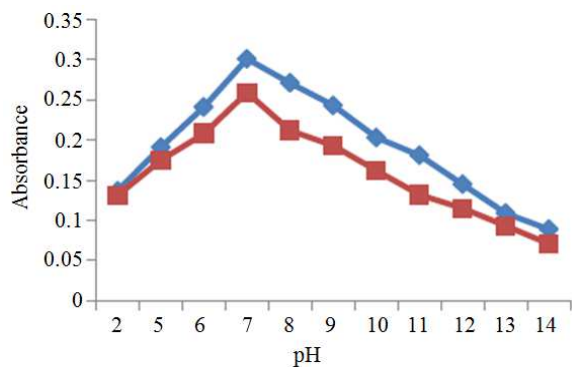

Fig. 7. Effect of pH on the cloud point extraction of $Mn^{+2} = 16$ $\mu g\ L^{-1}$ and $Hg^{+2} = 14\ \mu g\ L^{-1}$, HTMCDAP = 7×10^{-5} Mol L^{-1}, 0.8 mL 10% (V/V) (Triton X-100)
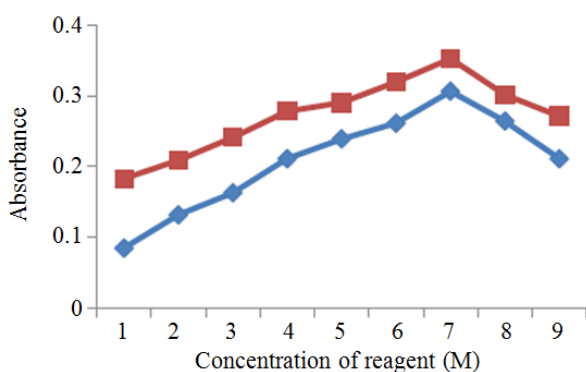

Fig. 8. Effect of HTMCDAP concentration on the cloud point extraction of $Mn^{+2} = 16\ \mu g\ L^{-1}$ and $Hg^{+2} = 14\ \mu g\ L^{-1}$, 1 0.8 mL 10%(V/V) (Triton X-100), pH = 7
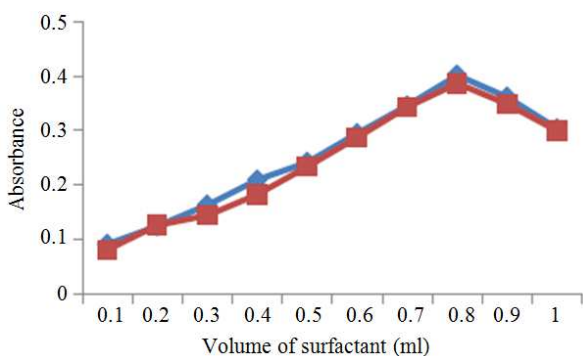

Fig. 9. Effect of volume 10%(v/v) TritonX-100 on the cloud point extraction of Mn+2 = 16 $\mu g\ L^{-1}$ and $Hg^{+2} = 14\ \mu g$ L^{-1}, HTMCDAP = 7×10^{-5} Mol L^{-1} pH = 7
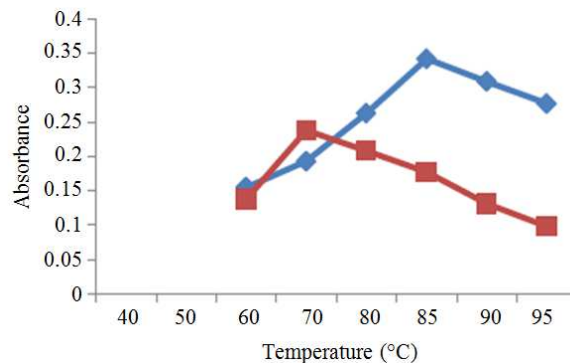

Fig. 10. Effect of the temperature on the cloud point extraction of $Mn^{+2} = 16$ $\mu g\ L^{-1}$ and $Hg^{+2} = 14$ $\mu g\ L^{-1}$, HTMCDAP = 7×10^{-5} Mol L^{-1} pH = 7
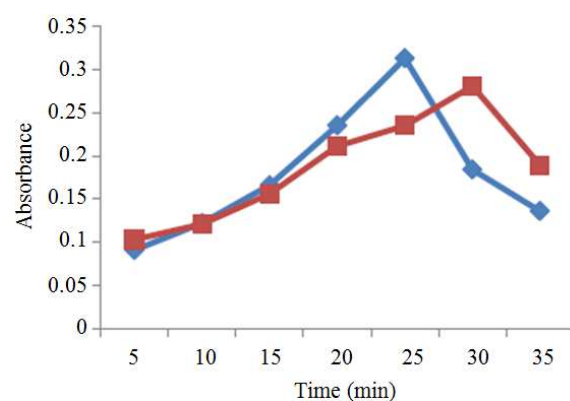

Fig. 11. Effect the incubation of time on the cloud point extraction of $Mn^{+2} = 16\ \mu g\ L^{-1}$ and $Hg^{+2} = 14\ \mu g\ L^{-1}$, HTMCDAP = 7×10^{-5} Mol L^{-1} pH = 7

Table 3. Effect of Interference ions

Interfering ion	Amount added $\mu g\ L^{-1}$	Percentage of Interference (%) of reagent
K^+	150	+2.88
Na^+	150	+4.52
Ca^{+2}	150	+10.6
Mg^{+2}	150	+7.40
SCN^-	150	-5.3
Br^-	150	--12.75
So_4^{-2}	150	-14.4
I^-	150	--9.0
$Cr_2O_7^{-2}$	150	100

Table4. Analytical characteristics data of the proposed method

Parameter	Hg (II)	Mn(II)
λ_{max}	423 nm	444 nm
R2	0.9982	0.9961
RSD	1.3%	1.4%
Linear rang	2-14 $\mu g\ L^{-1}$	2-16 $\mu g\ L^{-1}$
Recovery	96-98.7%,	97-99.7%
Limit of detection	0.75 $\mu g\ L^{-1}$	0.4 $\mu g\ L^{-1}$
Slope	0.0278	0.0252
Intercept	0.0144	0.0129

Accuracy and Precision

The accuracy and precision of proposed methods were determined Hg (II) and Mn (II) at two concentration level of by analyzing eight replicate sample of each concentration. Table 5 show high reproducibility of results and precision of the methods.

Analytical Application

The proposed methods was applied to the quantitative determination of Hg (II) and Mn(II) in wastewater of Rustimiyah city in Iraq. It was gave a good accuracy and precision as shown in Table 6.

Table 5. Accuracy and precision of proposed methods

Amount of Hg(II) µg L^{-1}

Present	Found	RSD (%)*	Recovery (%)
14	13.78	1.40	96.0
6	5.88	1.20	98.7
Amount of Mn(II) µg L^{-1}			
16	15.87	1.55	97.0
6	5.91	1.30	99.7

*Average of eight determination

Table 6. Application of proposed method for determination Hg (II) and Mn(II)

	Real sample	Taken	Found	RSD (%)*	RSD % average	Recovery (%)	Recovery (%) average
Hg(II)	Wastewater (input)of Rustimiyah city	14	13.880	0.8	0.65	99.0	97.5
		6	5.760	0.5		96.0	
	Wastewater (output) of Rustimiyah city	14	13.650	0.9	0.80	97.5	95.0
Mn(II)		6	5.590	0.7		93.0	
	Wastewater (input)of Rustimiyah city	16	16.051	1.1	0.95	100.0	100.0
		6	6.049	0.8		100.0	
	Wastewater (output) of Rustimiyah city	16	16.059	1.3	0.95	100.0	100.5
		6	6.061	0.6		101.0	

Table 7. Comparison of the proposed method with reported methods for the preconcentration and CPE of Hg (II) and Mn(II)

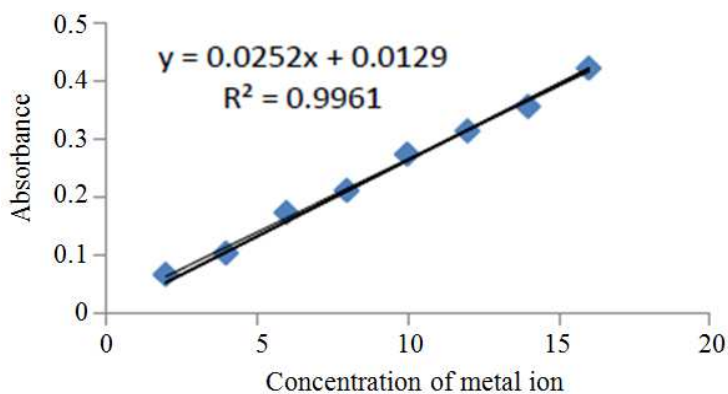| Element	Chelating agent	Surfactant	Technique	Linear range	RSD%	The detection limits	Ref.
Mn(II)	PMBP	TritonX-100	FAAS			1.45 ng mL^{-1}	Sun *et al*. (2006)
Hg(II)	PAN	TritonX-114				1.65	Ulusoy *et al*. (2012)
Mn(II)	TAN	TritonX-114		0.28	_		Toe and Chen (2001)
Mn(II)	MPBIM	Triton X-114	AAS			1.47	Shokrollahi *et al*. (2011)
Hg(II)	Methyl green	TritonX-100	ICP-OES			0.065	Li and Hu (2007)
Hg(II)	3-NBT	TritonX-114	ICP-OES			0.48	Shoaee *et al*. (2012)
Mn(II)	2-[2′-(6-methylben-zothiazolylazo)]-4-bromophenol	TritonX-100	FI-FAAS			0.70	Lemos and David (2010)
Hg(II) Mn(II)	HTMCDAP	TritonX-100	UV/VIS	2-14 µg L^{-1}	1.3%	0.75 µg L^{-1}	Proposed
				2-16 µg L^{-1}	1.4%	0.4 µg L^{-1}	methods

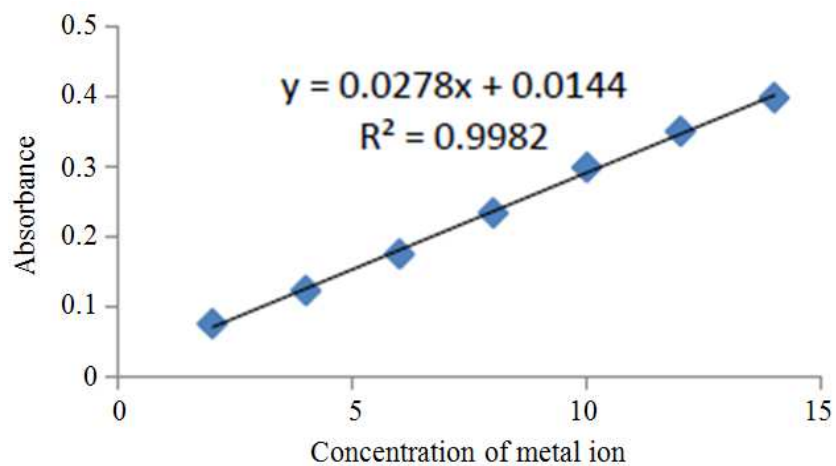
Fig. 12. Calibration graph of Mn(II)
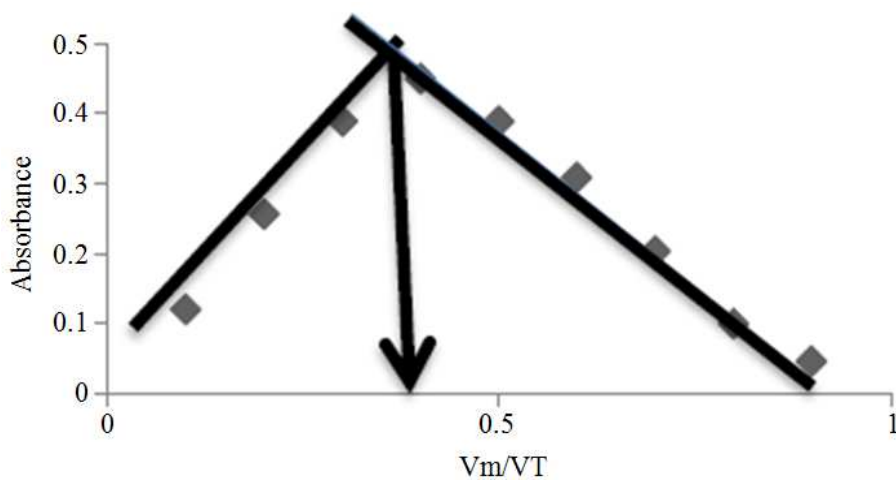
Fig. 13. Calibration graph of Hg (II)

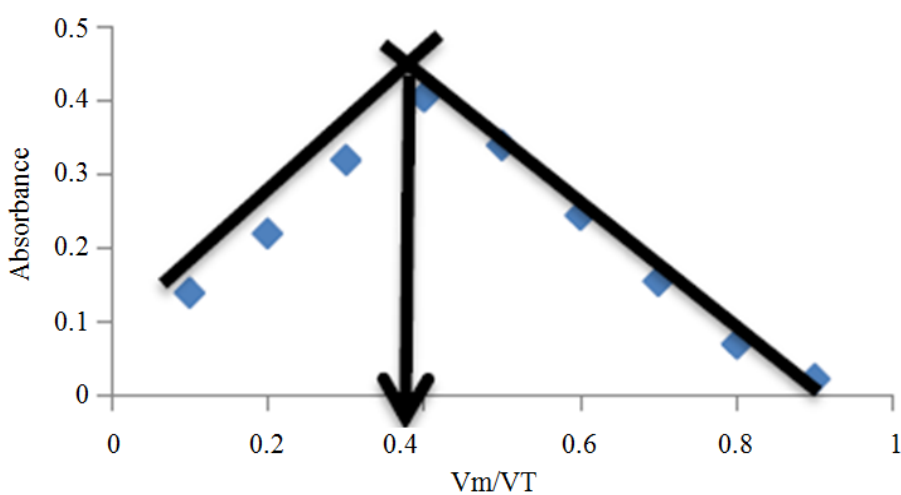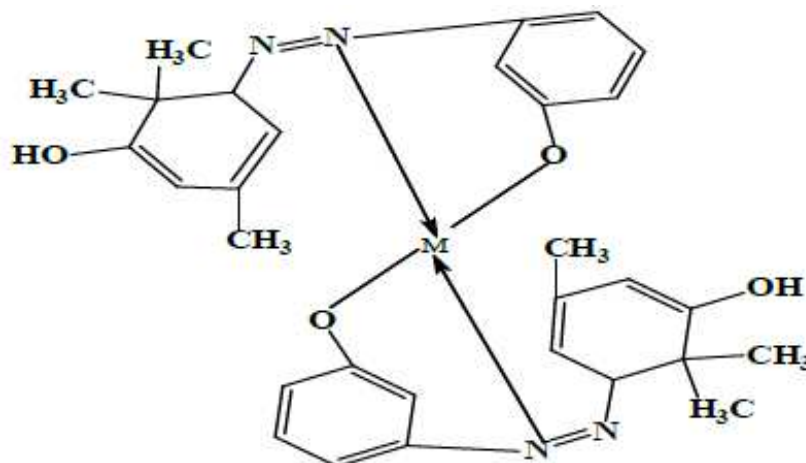Fig. 14. Continuous variation of Hg^{+2}-HTMCDAP

Fig. 15. Continuous variation of Mn^{+2}-HTMCDAP

Scheme2. The predictable structure of Mn^{+2}- HTMCDAP and Hg^{+2}- HTMCDAP

Conclusion

Cloud point extraction is cheapens, easy, safe and versatile pre-concentration technique to determine Hg(II) and Mn(II) by UV/VIS. In proposed method the ligand HTMCDAP is a sensitivity and selectivity for determination of Hg(II) and Mn(II) in wastewater sample and gave a good RSD and low limit of detection.

Acknowledgment

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Ethics

This article is original and contains unpublished material. The corresponding author confirms that all of the other authors have read and approved the manuscript and no ethical issues involved.

References

Ahmad, F., K. Niknam, I.E. Niknam, S. Delavari and A. Khanmohammadi, 2011. Cloud point extraction and determination of silver ion in real sample using Bis((1H-benzo[d]imidazol-2yl)methyl)sulfane. Chemistry, 8: 435-442. DOI: 10.1155/2011/180476

Al-Bayati, S.M., E.M. Rasheed, M.A. Al-Soodani and S.M. Salah, 2013. Synthesis, characterization and stability study of V(IV), Zr(IV), Rh (I II), Pd (II), Cd(II) and Hg(II) complexes with pyrazol derivative. Baghdad Sci. J., 11: 1592-1603.

Bakir, S.R. and S.A. Dhahir, 2013. Cloud point extraction spectrophotometric determination of trace amounts of nickel by SALEN as reagent in waste water of Iraq. Int. Interdisciplinary Res. J., 3: 9-21.

Chen, J. and K.C. Toe, 2001. Determination of cadmium, copper, lead and zinc in water samples by flame atomic absorption spectrometry after cloud point extraction. Anal. Chim. Acta, 450: 215-222. DOI: 10.1016/S0003-2670(01)01367-8

Dhahir, S.A. and S. RhajabBakir, 2015. Cloud point extraction spectrophotometric determination of nickel, copper, cobalt and chromium by 4- HBDA1, 5DPHP as reagent in wastewater of Iraq. Environ. Sci., 10: 150-160.

Doroschuk, V.O., S.O. Lelyushok, V.B. Ishchenko and S.A. Kulichenko, 2004. Flame atomic absorption determination of manganese(II) in natural water after cloud point extraction. Talanta, 64: 853-856. DOI: 10.1016/j.talanta.2004.03.056

Kirkan, B. and R. Gup, 2008. Synthesis of new azo dyes and copper(II) complexes derived from barbituric acid and 4-aminobenzoylhydrazone. Turk. J. Chem., 32: 9-17.

Lemos, V.A. and G.T. David, 2010. An on-line cloud point extraction system for flame atomic absorption spectrometric determination of trace manganese in food samples. Microchemcal J., 94: 42-47. DOI: 10.1016/j.microc.2009.08.008

Li, Y. and B. Hu, 2007. Sequential cloud point extraction for the speciation of mercury in seafood by inductively coupled plasma optical emission spectrometry. Spectrochimica Acta Part B: Atomic Spectrometry, 62: 1153-1160. DOI: 10.1016/j.sab.2007.07.005

Manzoori, J.L. and H. Abodlmohammad-Zadeh, 2007. Extraction and preconcentration of lead using cloud point methodology: Application to its determination in real samples by flame atomic absorption spectrometry. Acta Chim. Slov., 54: 378-384.

Manzoori, J.L. and A. Bavili-Tabrizi, 2002. The application of cloud point preconcentration for the determination of Cu in real samples by flame atomic absorption spectrometry. Microchem. J., 72: 1-7. DOI: 10.1016/S0026-265X(01)00113-8

Mohammed, I.A. and M. Asniza, 2010. Synthesis of new azo compounds based on N-(4-hydroxypheneyl)maleimide and N-(4-methylpheneyl)maleimide. Molecules, 15: 7498-7508. DOI: 10.3390/molecules15107498

Nakamoto, K., 1997. Infrared and Raman Spectra of Inorganic and Coordination Compounds, Theory and Applications in Inorganic Chemistry. 5th Edn., Wiley, ISBN-10: 0471163945, pp: 408.

Portugal, L.A., H.S. Ferreia, W.N.L. dos Santos and S.L.C. Ferreia, 2007. Simultaneous pre-concentration procedure for the determination of cadmium and lead in drinking water employing sequential multi-element flame atomic absorption spectrometry. Microchim. J., 87: 77-80. DOI: 10.1016/j.microc.2007.05.008

Roundhill, D.M., I.B. Solangi, S. Memon, M.I. Bhanger and M. Yilmas, 2009. The liquid liquid extraction of toxic metals (Cd, Hg and Pb) by calixarenes. Pak. J. Anal. Environ. Chem., 10: 1-13.

Scarmoutzos, L.M. and O.E. Boyd, 2004. Environmental and toxicological concerns of dental amalgam and mercury. MVS Solutions, Inc.

Shoaee, H., M. Roshdi, N. Khanlarzadeh and A. Beiraghi, 2012. Spectrochim. Acta Part A: Molecular Biomolecular Spectroscopy, 98: 70-75. DOI: 10.1016/j.saa.2012.08.027

Shokrollahi, A., H. Tavallali, Z. Montaseri and K. Nikanam, 2011. Using an indol derivative as complexing agent for cloud point preconcentration and determination of magnesium and silver ions in various samples by faas. J. Chil. Chem. Soc., 2011, 57: 1134-1139.
DOI: 10.4067/S0717-97072012000200017

Sun, Z., P. Liang, Q. Ding and J. Cao, 2006. Cloud point extraction preconcentration of manganese(II) from natural water samples using 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone and triton X-100 and determination by flame atomic absorption spectrometry. Anal. Sci., 22: 911-913.
DOI: 10.2116/analsci.22.911

Toe, K.C. and J. Chen, 2001. Determination of manganese in water samples by flame atomic absorptionspectrometry after cloud point extraction. Analyst, 126: 534-537. DOI: 10.1039/B008717N

Ulusoy, H.I., R. Gurkan and S. Ulusoy, 2012. Cloud point extraction and spectrophotometric determination of mercury species at trace levels in environmental samples. Talanta, 88: 516-523.
DOI: 10.1016/j.talanta.2011.11.026

Veerachalee, N., V. P. Taweema and A. Songsasen, 2007. Complexation and spectrophotometric determination of cobalt(II) ion with 3-(2′-thiazolylazo)-2,6-diaminopyridine. Kasetsart J. (Nat. Sci.), 41: 675-680.

Velasco-Ryenolda, C., M. Navarro-Alarcón, H.L.G. De La Serranaa, V. Perez-Valero and M.C. Lopez-Martinez, 2008. Total and dialyzable levels of manganese from duplicate meals and influence of other nutrients: Estimation of daily dietary intake. Food Chem., 109: 113-121.
DOI: 10.1016/j.foodchem.2007.12.025

Wuilloud, G.M., J.C.A. de Wuilloud, R.G. Wuilloud, M.F. Silva and R.A. Olsina et al., 2002. Cloud point extraction of vanadium in parenteral solutions using a nonionic surfactant (PONPE 5.0) and determination by flow injection-inductively coupled plasma optical emission spectrometry. Talanta, 58: 619-627. DOI: 10.1016/S0039-9140(02)00366-1

Yang, G., Z. Xia, Y. Wu, H. Sun and J. Yin, 2004. Study on the solid phase extraction of Hg(II)-SBDTR chelate with C_{18} disks and its application to the determination of mercury in tobacco and tobacco additive. Bull. Korean Chem., 25: 549-553.

Youcef, M.H., T. Benabdallah and H. Ilikti, 2006. A study on copper (II) extraction from sulphate medium via cloud- point extraction with N-salicylideneaniline ligand in presence of non-ionic surfactant. Can. J. Anal. Sci. Spect., 51: 267-277.