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-thiazolyloazo)-2-naphthol(TAN)(Chen and Toe, 2001), 2-(5-bromo-2pyridylazo)-5-diethylaminophenol(5-Br-PADAP) (Wuilloud et al., 2008), -(2-thiazolyloazo)-p-cresol (TAC) (Portugal et al., 2007), (2-pyridylazo) resorcinol (PAR) (Doroschuk et al., 2004), FMBP (Manzoori and Abodlmohammad-Zadeh, 2007) and Schiff base such as N,N’-bis (salicylidene) ethylenediamin [SALEN] (Bakir and Dhahir, 2013), E-4-(3-hydroxybenzyldieneamino) 1,5 dimethyl-2-phenyl-1Hpyrazol- 3(2H)-one[4-(HBDA1), 5DPHPO] (Dhahir and RhajabBakir, 2015), Bis((1H-benzo[d]imidazol-2-yl) methyl) sulfane[BHIS] (Ahmad et al., 2011), N-salicyclideneaniline (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 monohydrate 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 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 \(\lambda_{max}\) 444 and 423 nm.

Synthesis and Characterization of Reagent

The synthesis of 3-[(5-hydroxy-3,6,6-trimethylclohexa2,4-dienyl)diazeyl]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 at1438 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.

Ultraviolet 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 (π→π*), 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](image)
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 | Calculation |
|------------|------------|--------|-------------|
|            | C          | H      | N          | S  |                  |
| 69.74      | 7.02       | 10.84  | 0.0        | 0.0 | Theoretical |
| 70.76      | 6.93       | 11.11  | 0.0        | 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 µg L$^{-1}$ and Hg$^{2+}$ = 14 µg 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 µg L$^{-1}$ and Hg$^{2+}$ = 14 µg L$^{-1}$, pH = 7

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

Table 3. Effect of Interference ions

| Interfering ion | Amount added µg 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$_2$O$_7^{2-}$ | 150                     | 100                                      |

Table 4. Analytical characteristics data of the proposed method

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

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

Analytical Application

The proposed methods were applied to the quantitative determination of Hg (II) and Mn(II) in wastewater of Rustimiyah city in Iraq. It was found that these methods 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 (%) |
|-------------|-------|-------|----------|---------------|--------------|--------------|
| Hg(II)      | Wastewater (input) of Rustimiyah city | 14     | 13.80    | 0.8           | 0.65         | 99.0         | 97.5        |
|             |       | 6     | 5.760    | 0.5           | 96.0         |              |             |
| Mn(II)      | Wastewater (output) of Rustimiyah city | 14    | 13.650   | 0.9           | 0.80         | 97.5         | 95.0        |
|             |       | 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 | 1.65 | Ulusoy et al. (2012)        |
| Hg(II)  | PAN             | TritonX-114| FAAS      | 1.45 ng mL⁻¹ | 0.28 | Sun et al. (2006)           |
| Mn(II)  | TAN             | TritonX-114| FAAS      | 1.45 ng mL⁻¹ | 0.28 | Tou et al. (2001)           |
| Mn(II)  | MPBIM           | TritonX-114| AAS       | 1.45 ng mL⁻¹ | 0.28 | Shokrollahi et al. (2011)   |
| Hg(II)  | Methyl green    | TritonX-100| ICP-OES   | 0.065        | 0.48 | Li and Hu (2007)            |
| Hg(II)  | 3-NBT           | TritonX-114| ICP-OES   | 0.065        | 0.48 | Shoaee et al. (2012)        |
| Mn(II)  | 2-[2′-(6-methylbenzothiazol-2-yloazo)-4-bromophenol | TritonX-100| FI-FAAS   | 0.065        | 0.48 | Lemos and David (2010)      |
| Hg(II)  | Mn(II)          | HTMCDAP    | TritonX-100| UV/VIS      | 0.065| Proposed                    |

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.

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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.

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