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Facile spectrophotometric determination of Cd(II) and Pb(II) using murexide reagent in mixed solvent system

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ABSTRACT

The spectrophotometer method was employed to determine the trace level of hazardous elements (cadmium and lead). Murexide interacts with Cd(II) and Pb(II) in slightly acidic and basic solutions (pH 3-9) to form orange to reddish orange chelates with absorbance maxima at 483 and 504 nm. The reaction is rapid, and the absorbance remained constant for more than three hours. The average molar absorptivity and sensitivity values for Cd and Pb were determined to be (11856 $L.mol^{-1}.cm^{-1}$ and 0.107 ppm^{-1}) and (2422 $L.mol^{-1}.cm^{-1}$ and 0.061 ppm^{-1}), respectively. Linear calibration curves for 0.5-7.0 $mg.L^{-1}$ Cd and 0.75-12.0 ppm Pb were produced. The chelate's stoichiometric composition was 1:2 (metal ion: murexide) except for Pb in the 6:4 proportion, which had a 1:1 mole ratio. Moderate levels of some interfering ions have no effect on the determination of Pb(II) and Cd(II) ions.

Capsule Summary: Using murexide indicator, a direct and easy spectrophotometric methodology for determining cadmium and lead ions was performed with detection limits of 37 and 171 ppb, respectively.

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INTRODUCTION

Heavy metals are a significant class of contaminants that come from both point and diffuse sources (e.g., sludge dumping, industrial effluents, mine tailings) (Capone et al., 1983). Its increasing use in various industries such as storage batteries, gasoline, cable manufacturing, paint industry motorization, and increasing use of communal and industrial wastewater for liming and fertilizing soil, as well as long-term use of some pesticides, may result in excessive concentrations of lead, cadmium, zinc, copper, or mercury in the soil, and ammunition have resulted in recurring environmental contamination through developing and industrialized areas of the world (Yaghi et al., 2022; Alsamarrai, 2011).

Cadmium is a common hazardous element found naturally in the environment. People exposed to cadmium through the air, food, and water risk serious health hazards, including kidney, liver, and lung failure. Furthermore, significant damage to the cardiovascular, immunological, and reproductive systems was seen (Fowler, 2009). Cadmium is efficiently retained in the kidney (half-life of 10-30 years), and its concentration in the urine is proportionate to its concentration in the blood (Alkherraz et al., 2019; Kumar et al., 2016).

Lead is a toxin that accumulates in the body through lead water pipes, lead-based paints, and leaded gasoline.

Even tiny amounts of Pb (II) in environmental samples cause pollution and a number of deadly disorders, including renal blood and neurological system failure (Khan and Ahmed, 2006). Lead toxicity has been widely investigated. Human lead poisoning causes serious damage to the kidneys, liver, brain, reproductive system, and central nervous system, and can result in death (Zaky et al., 2017; Elsherif and Aljaroushi; 2021).

The voltammetry (Mahesar et al., 2010), electrochemical methods (Bui et al., 2012), atomic absorption spectroscopy (AAS) (Elsherif and Kuss, 2012a), inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Elsherif and Kuss, 2012b), and inductively coupled plasma optical emission spectroscopy (ICP-OES) (Zhu and Chiba, 2012) have been reported for the determination of Cd(II) and Pb(II) in real matrices. Such approaches often include modification processes and are more expensive to measure. Among them, spectrophotometric techniques are inexpensive and simple to use, with comparable sensitivity (Kong et al. 2010).

Numerous chelating substances have previously been reported for the analysis of Cd(II) and Pb(II) in various environmental matrices, including derivatives of sulphonic acid, luminol, resorcinol, naphthol, amino phenols, amino benzene, quinolinol, hydroxy quinoline, dibromo-p-methyl-carboxy sulfonazo 5 , chlorophosphonazo(III) (Zhai et al., 2013; Ahmed et al., 2008; Fang et al., 2002; Pan et al., 2003), and thiosemicarbazones derivatives has been used for the determination of Cd(II) and Pb(II) in several environmental matrices (Reddy et al., 2011).

The structure of the reddish-purple compound murexide is seen in Figure 1. Due to its usage in the disciplines of spectrophotometry and chemical analysis, it has attracted a lot of attention (Grudpan et al., 1998). It functions as a metal ion indicator and is frequently used in standard EDTA titrations. It is furthermore employed as a chromogenic reagent in several metals' traditional spectrophotometric determination (Masoud et al., 2006; Elsherif et al., 2022).

However, the stability constants of murexide complexes with most metal ions are not especially large which may limit murexide's applicability as a metallochromic indicator in aqueous solutions. We were interested in how solvent properties affected the stoichiometry and stability of murexide complexes with Cd(II) and Pb(II) (Elsherif et al., 2020a).

Thus, in this study, the spectrophotometric method was utilized to analyze Cd(II) and Pb(II). These metal ions react with the murexide indicator to form coloured complexes. Many desired aspects, such as pH effect, reaction duration, and solvent mixture proportion, were monitored to enhance the sensitivity of the approach.

MATERIAL AND METHODS

Apparatus, chemical and reagents

For absorbance measurements, an Agilent Cary 60 UV/Vis spectrophotometer from Agilent Technologies Australia was used, and pH was adjusted with a (JENWAY pH-meter, Model 3510) coupled with a combination glass-calomel electrode.

All chemicals utilized were either analytical-reagent grade or the highest accessible. Throughout, double-distilled de-ionized water, which is non-absorbent to UV light, was employed. Glass containers were cleaned by immersing them in acidified 10% (w/w) HNO_3 solutions and then rinsing them many times with high-purity de-ionized water. In a polypropylene container holding 1 ml of concentrated HNO_3, stock solutions and environmental water samples (1000 ml each) were stored.

Murexide solution

To make this solution, dissolve the required amount of murexide salt (Aldrich ACS grade) in a known volume of distilled de-ionized water. As needed, more dilute reagent solutions were produced.

Cd(II) and Pb(II) standard solutions

Dissolving 77.1 and 82.8 mg of cadmium nitrate and lead nitrate (Merck proanalysis grade) in doubly distilled de-ionized water produced a 50-ml stock solution ($5x10^{-3}$M) of divalent cadmium and lead. To avoid hydrolysis, one ml of diluted nitric acid was added to the stock solution. More dilute standard solutions were made as needed.

Process variables effect

In order to investigate the effect of the effect acidity on the absorbance of the complex, experiments were made w by mixing equal volumes of metal ion and ligand solutions, a series of 25 ml solutions was produced. 0.1 M hydrochloric acid and sodium hydroxide solutions were used to adjust the pH of the solutions. To investigate the influence of pH, the absorbance of the solutions was measured at the optimal wavelength. The complexes solution was produced by mixing equal volumes of the metal ion and ligand solutions, then monitoring the absorbance of each complex at intervals (every 5 min) and up to 180 min to examine the effect of time on the stability of the prepared complexes.

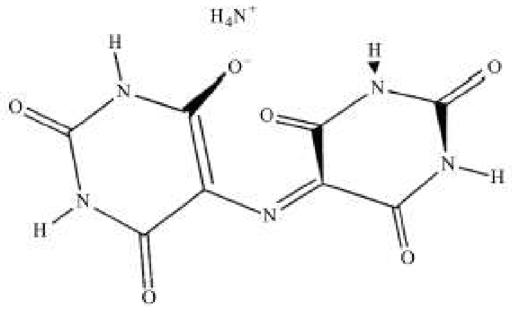
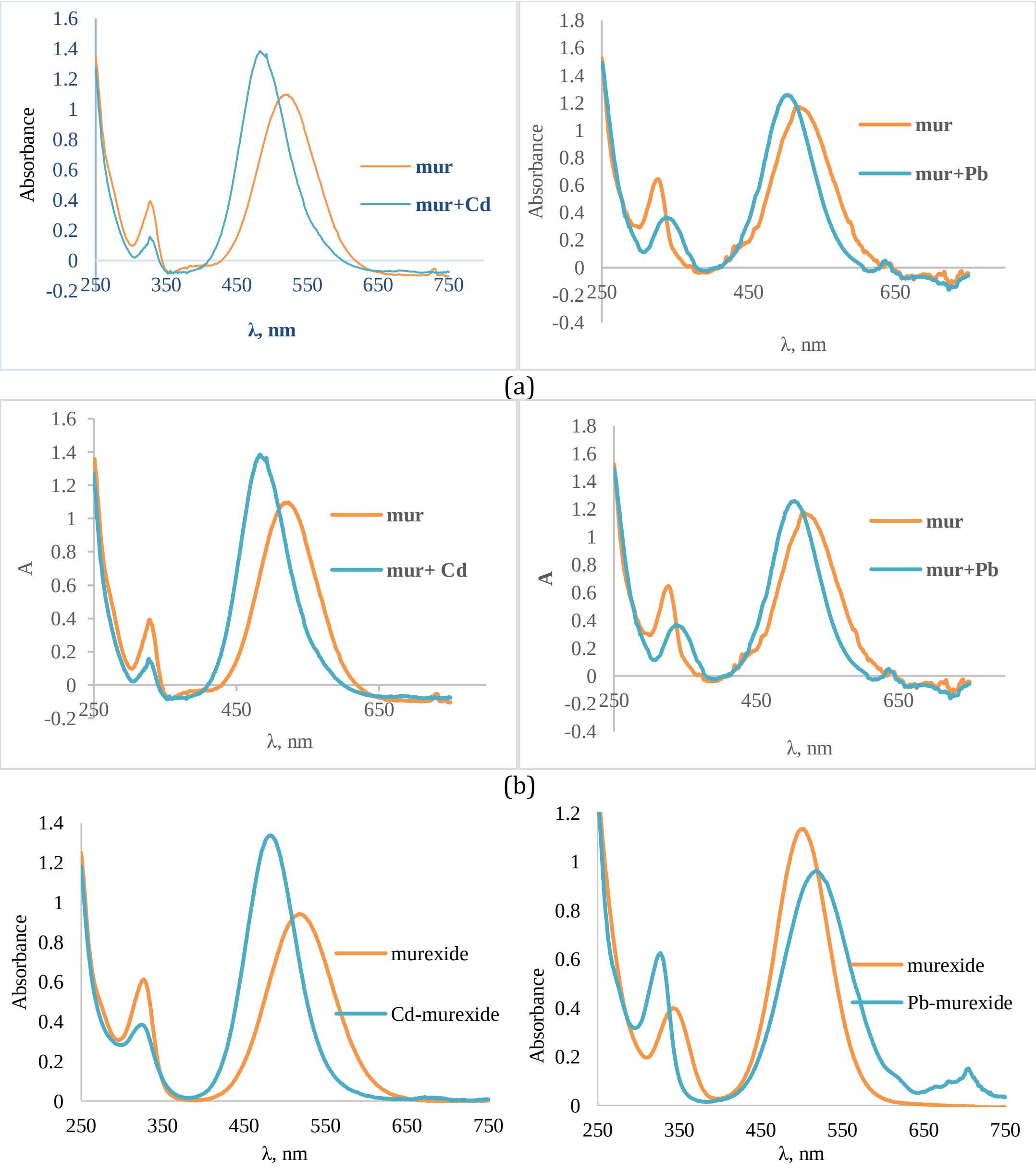


Fig. 1: Structure of murexide



(a)

(b)

(c)

Fig. 2: Absorption spectra of Cd(II) and Pb(II) complexes in three different mixed solvents of water: isopropanol; (a) 8:2 (b) 6:4 (c) 3:7

Complex composition and stability

Job's (18) approach of continuous variations, as expanded by Vosburgh and Cooper, is a relatively fast and good approach for determining the composition of the primary complex formed in a given concentration range of the reactants (Elsherif et al., 2020b). Also, to determine the stability constant of the synthesized complexes, the modified Job approach was used.

Calibration curve

To determine the system's adherence to Beer's law, the following calibration curve was established: A series of 25 ml volumetric flasks were filled with varied amounts of cadmium and lead solutions (5x10^{-3} M), a fixed volume of murexide (5x10^{-3} M), the pH was adjusted, and the solutions were diluted to the mark with double distilled water. After approximately 5 minutes, the absorbance of each solution at optimal wavelength was measured against a reagent blank that had been handled similarly. The results revealed a linear connection between metal ion concentration and absorbance, which was used to calculate method sensitivity.

Effect of foreign ions

The absorbance of solutions containing a given quantity of cadmium and lead was found to be affected by the content of various salt solutions (0.01, 0.02, 0.05, 0.1, 0.2, 0.5 M). By altering the concentration of salt solutions, this impact was investigated (Cl^-, NO_3^-, SO_4^{-2}, CH_3COO^-). The addition of HCl or NaOH kept the pH of the solution constant at its optimal value.

RESULTS AND DISCUSSION

Absorption spectra

Figure 2 depicts the absorption spectra of murexide and its cadmium and lead complexes in three different ratios of water and isopropanol combined solvents (8: 2, 6: 4, 3: 7).

As can be observed, the resultant complexes are all recognized by a rather substantial shift towards shorter wavelengths when compared to the free ligand. In general, the electrostatic interaction of a bonded metal ion would not have such a strong influence on the electronic structure of a dye molecule, and hence on its spectrum. The bending of the murexide molecule's two rings relative to one other (around the N-bridge axis) caused by metal ion complexation is thought to be responsible for such spectral behaviour (Fat'hi and Shamsipur, 1993). It is also observed that the shift that happens in the case of cadmium ion is larger, which is due to the cadmium ions has a lower size than that of lead. The cadmium and lead complexes' highest absorptions occurred at 483 and 503 nm, respectively. There is a significant overlap between the ligand spectra and the spectrum of the lead ion complex. However, the complex's absorption intensity was the greatest among all examined mixed solvents (except for the ratio 3:7 with lead complex).

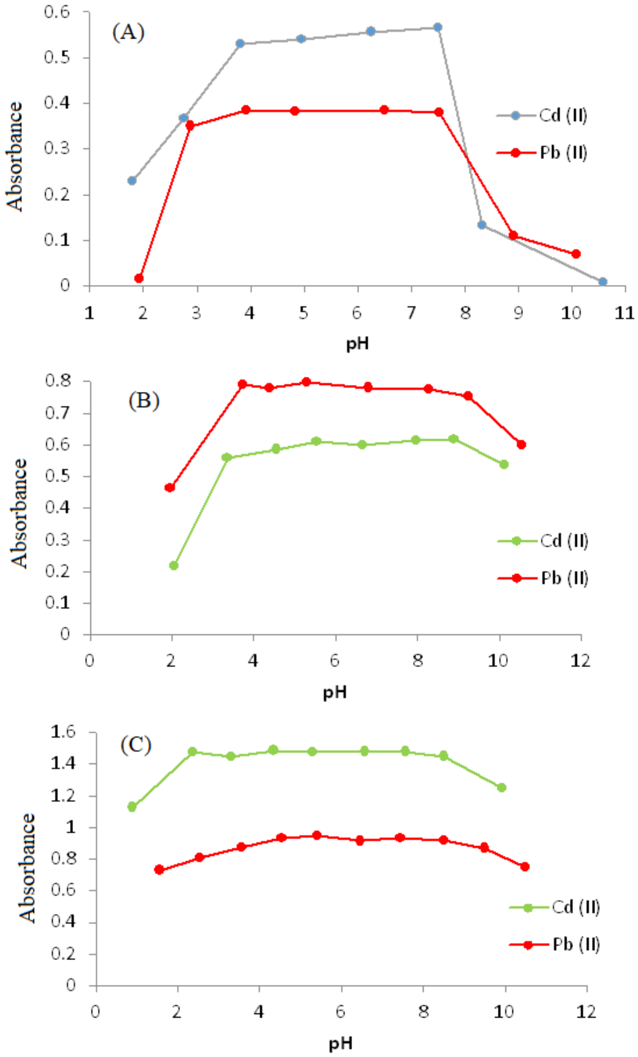


Fig. 3: Absorption spectra of Cd(II) and Pb(II) complexes in three different mixed solvents of water: isopropanol; (a) 8:2 (b) 6:4 (c) 3:7

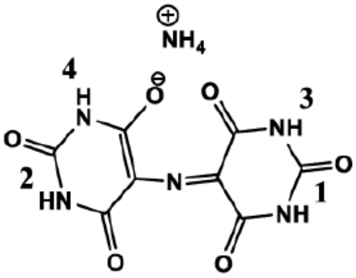


Fig. 4: The four protons of murexide as a weak acid, (Zaky et al., 2017).

Effect of acidity

The examination of the influence of pH on the color intensity of the complexes revealed that the appropriate pH ranges for cadmium and lead were (4-7.5 and 3-7.5 for 8:2 ratio), (4-9 and 3-9 for 6:4 ratio), and (3-9 and 2-10 for 3:9 ratio), as shown in Figure 3.

pH is a significant factor that influences the formation of metal complexes since all ligands are weak acids or bases that may be protonated or deprotonated depending on the pH of the solution. Murexide is considered as a weak acid because it has four protons, as shown in Figure 4. These protons completely ionize in basic media due to relatively weak ionization constants (pk_{a1}=9.2, pk_{a2}=10.5) (Zaky et al., 2017). In a very acidic medium, murexide dissociates into uramil and alloxan (Elsherif et al., 2022). Protonation, which makes nonbonding electron-pairs unavailable for complexation and hence lowers the tendency to form complexes with metal ions, limits the ligand's ability to react with metal ions. As a result, the pH of the solution may change the complex formation equilibrium. The precipitation of metal ions as hydroxide at higher pH (pH>9 in this study) impacts the ideal pH for complexation as a second factor.

Effect of reaction time

Because certain complexes are unstable and may dissociate after production, the study of complex stability throughout time is crucial. Following the production of the complex under ideal conditions, the absorbance values of the solutions were measured as a function of time. According to Figure 5, there was no change in absorbance over a period of three hours.

Effect of foreign ions

Study was done on how four ions: Cl^-, NO_3^-, SO_4^{-2}, and CH_3COO^- affected the complex formation reaction and the analysis of just 1 $mg.l^{-1}$ of cadmium and lead. The difference between the absorbance recovery value and the predicted value for both ions functioned as the interference criteria. The results are displayed in Figure 6. As can be shown, at low to moderate concentrations, the foreign ions have no significant influence on the detection of metal ions. Sulphate ions caused the most serious interferences. The precipitation of metal sulphate is most likely the cause of the sulphate ion interference (Ullah and Haque, 2010).

Stoichiometric ratio and stability constant

A series of solutions were made by combining an equimolar solution of Cd(II) and Pb(II) with ligand in various proportions ranging from 0.1 ml to 0.9 ml ($5.0x10^{-3}$ M) while maintaining the total moles constant. The metal-ligand ratio was calculated using a plot of absorbance at the specified wavelength vs ligand mole fraction. Figure 7 depicted the absorptance obtained for all complexes at a ratio of 1:2. (except for Pb in case of 6:4 ratio).

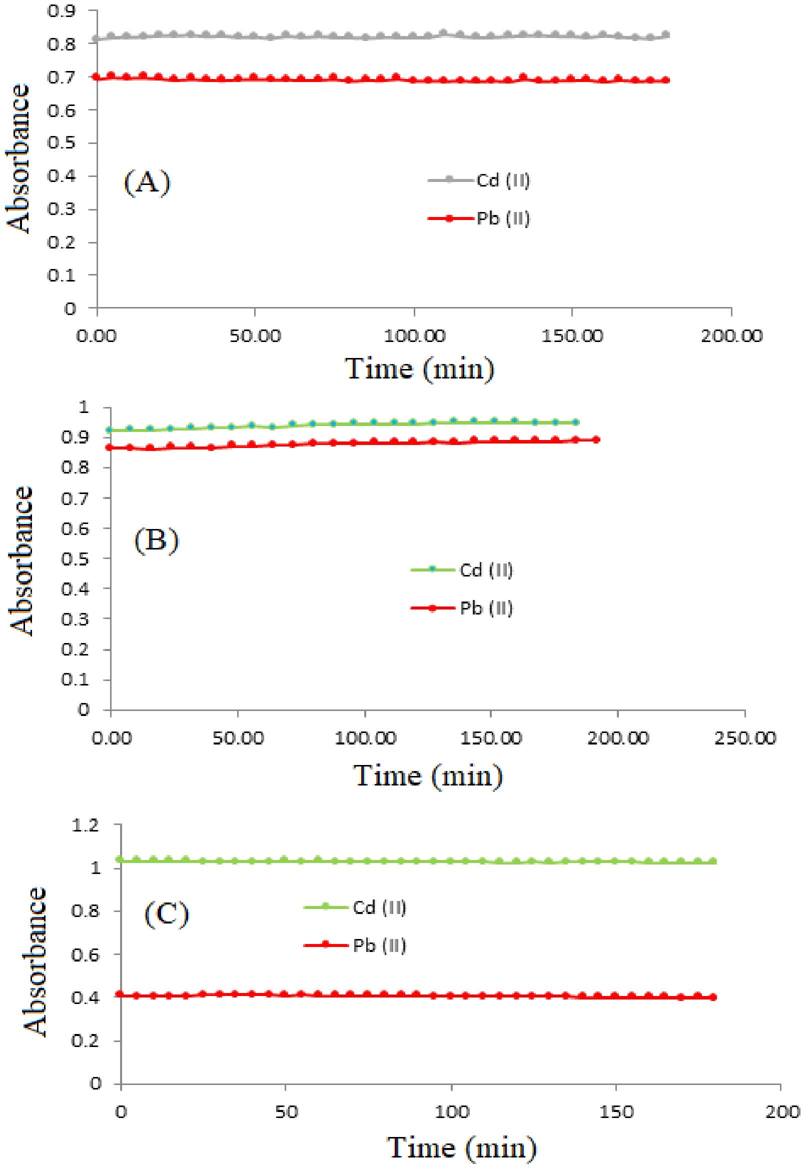


Fig. 5: Effect of time on absorption spectra of Cd(II) and Pb(II) complexes in three different mixed solvents of water: isopropanol; (a) 8:2 (b) 6:4 (c) 3:7

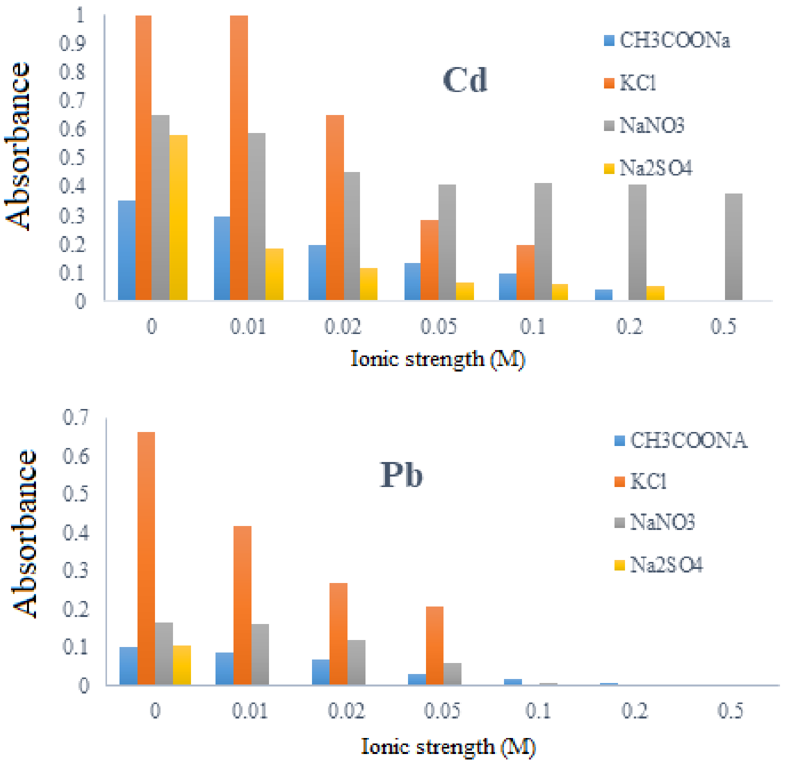


Fig. 6: Effect of foreign ions on absorption spectra of Cd(II) and Pb(II) complexes in mixed solvent of water: isopropanol (3:7)

Table 1: Parameters values of Cd-murexide complexes in three mixed solvent proportions

Ratio (water:isopro.)	λ_{max} (nm)	pH	L:M	Ɛ $l.mol^{-1}cm^{-1}$	$LogK_f$
8:2	483	4-7.5	2:1	19581	11
6:4	483	4-9	2:1	5703	11
3:7	483	3-9	2:1	11856	12

Table 2: Parameters values of Pb-murexide complexes in three mixed solvent proportions

Ratio (water:isopro.)	λ_{max} (nm)	pH	L:M	Ɛ $l.mol^{-1}cm^{-1}$	$LogK_f$
8:2	501	3-7.5	2:1	6689	13
6:4	502	3-9	1:1	2735	8
3:7	504	2-10	2:1	2422	14

Table 3: Selected analytical parameters obtained with the optimization experiments

Metal ion	DL ppm	QL ppm	Sensitivity ppm^{-1}	R^2	Linear range ppm
Cd(II)	0.037	0.122	0.107	0.999	0.50-7.0
Pb(II)	0.171	0.570	0.061	0.998	0.75-12.0

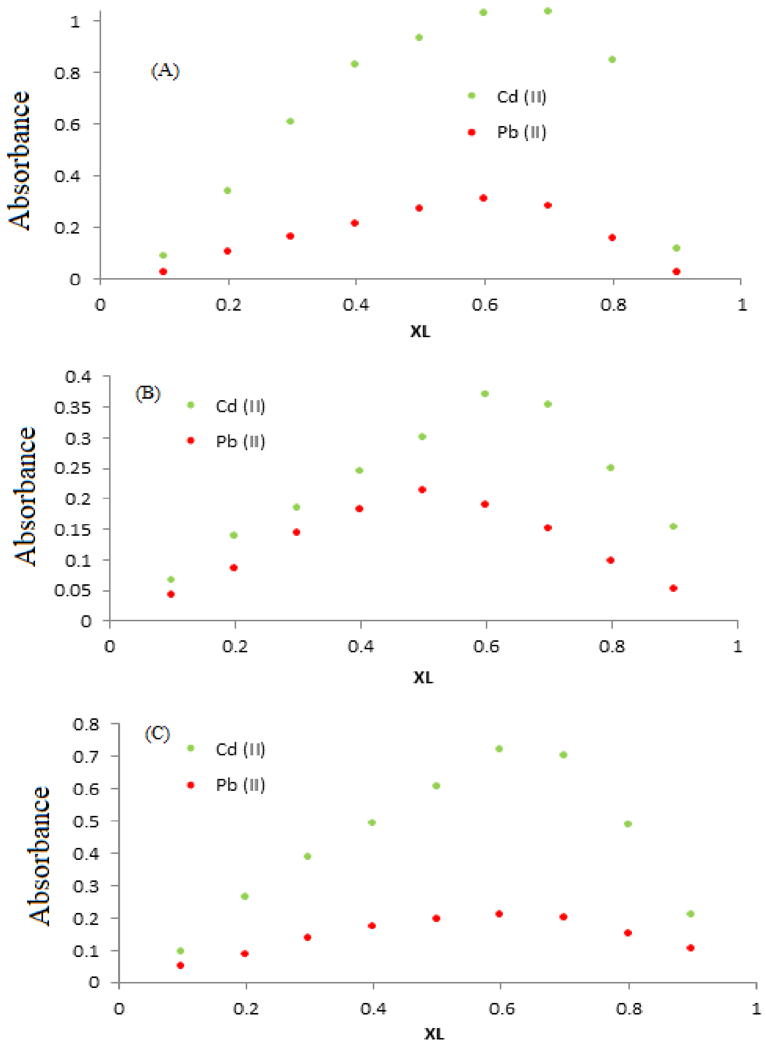


Fig. 7: Determination of the metal: reagent ratio of Cd(II) and Pb(II) with murexide complexes using continuous variation method at various mixed solvent ratios

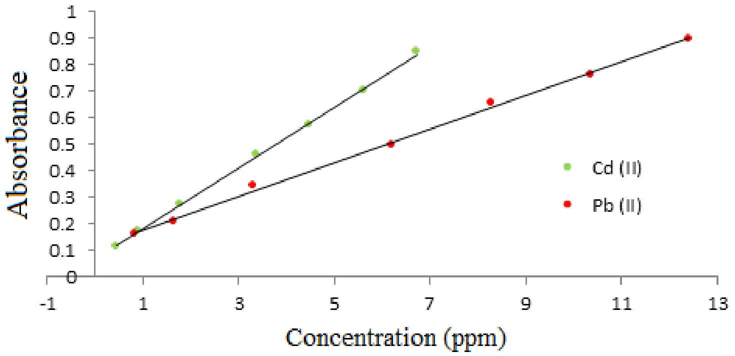


Fig. 8: Calibration graph of Cd(II) and Pb(II)

The molar absorptivity of the complexes at three different mixed solvent ratios may also be computed by taking the complex concentrations at each point and graphing the concentration vs the absorbance. The complex stoichiometry, stability constants, and molar absorptivity values are shown in Tables 1 & 2. The stability of the murexide complexes varies in the order Pb > Zn in all solvent mixtures tested. The similar arrangement has been described in the literature previously 1,3,14. The maximum stability reported for Pb(II) complexes among Cd(II) complexes is likely attributable to the cation's suitable ionic size, which might support a reasonable spatial fit with the murexide's flexible donating atoms (i.e. the bridging nitrogen atom and surrounding oxygen (Fat'hi and Shamsipur, 1993).

Calibration curves

Beer's law was used to develop the well-known equation for spectrophotometric analysis in very dilute solutions. The influence of metal concentration was investigated throughout a range of 0.1-20 mg. ml^{-1}, and the absorbance was linear for 0.5-7.0 mg.ml^{-1} cadmium at 483 nm and 0.75-12.0 mg.ml^{-1} lead at 504 nm. Sandell's sensitivity and limits of detection (Ojeda et al., 1987) [28] for cadmium and lead were determined to be (0.107 ppm^{-1} and 0.066 mg.l^{-1}) and (0.061 ppm^{-1} and 0.171 mg.l^{-1}), respectively. Figure 8 depicts a calibration curve that shows the limit of linearity range. Table 3 summarizes the selected analytical parameters acquired from optimization studies (Ojeda et al., 1987).

CONCLUSIONS

A new, simple, and reliable spectrophotometric approach for determining cadmium (II) and lead (II) was reported, based on the formation of a coloured complex between the metal ion and the murexide reagent in a mixed solvent of (3:7) water: isopropanol. For Cd(II) and Pb(II), the complex shows absorbance maxima at 483 and 504 nm, with molar absorptivity values of 11856 and 2422 L.mol^{-1}.cm^{-1}, respectively. The complex remained stable at room temperature for 72 minutes. The current method's sensitivity values are quite trustworthy for determining cadmium and lead in actual samples down to 122 and 570 ppb levels, respectively.

REFERENCES

Ahmed, M.J., Hossan, K.J., 2008. A rapid spectrophotometric method for the determination of cobalt in industrial, environmental, biological, pharmaceutical and soil samples using bis(5-bromosalicylaldehyde) orthophenylenediamine. Journal of the Iranian Chemical Society 5, 677-688.

Alkherraz, A.M., Hashad, O.M., Elsherif, K.M., 2019. Heavy Metals Contents in Some Commercially Available Coffee, Tea, and Cocoa Samples in Misurata City – Libya. Progress in Chemical and Biochemical Research 2(3), 99-107.

Alsamarrai, K.F., 2011. Spectrophotometric Assay of Lead in Human Hair Samples by using alizarin red (S) in Samarra area. Journal of University of Anbar for Pure Science 5(3) 1-8.

Bui, M.P., Li, C.A., Han, K.N., Pham, X.H., Seong, G.H., 2012. Electrochemical Determination of Cadmium and Lead on Pristine Single-walled Carbon Nanotube Electrodes. Analytical Sciences 28, 699-704.

Capone, D.G., Reese, D.D., Kiene, R.P., 1983. Effects of Metals on Methanogenesis, Sulfate Reduction, Carbon Dioxide Evolution, and Microbial Biomass in Anoxic Salt Marsh Sediments. Applied and Environmental Microbiology 45, 1586– 1591.

Elsherif, K.M., Aljaroushi, A.M., 2021. Assessment of Major and Minor Metals Levels in Selected Libyan Palm Dates Fruits. Journal of Applied Science and Environmental Studies 4(3), 446-459.

Elsherif, K.M., Hadidan, Q., Alkariwi, K., 2022. Spectrophotometric Determination of Zn(II) and Cu(II) in Analytical Sample Using Murexide Reagent. Progress in Chemical and Biochemical Research 5(3), 229-238.

Elsherif, K.M., Kuss, H-M., 2012a. Direct and Simultaneous Determination of Bismuth, Antimony, and Lead in Biological samples by Multi-Element Electrothermal Atomic Absorption Spectrometer. Der Chemica Sinica 3(3), 727-736.

Elsherif, K.M., Kuss, H-M., 2012b. Simultaneous Multi-Element Determination of Bismuth (Bi), Antimony (Sb), and Selenium (Se). Advances in Applied Science Research 3(4), 2402-2412.

Elsherif, K.M., Nabbra, F.M., Ewlad-Ahmed, A.M., Elkebbir, N., 2020a. Spectrophotometric Complex Formation Study of Murexide with Nickel and Cobalt in Aqueous Solution. To Chemistry Journal 5, 40-47.

Elsherif, K.M., Zubi, A., Shawish, H.B., Abajja, S.A., Almelah, E.B.M., 2020b. Complex Formation of Bis(salicylidene)ethylenediamine (Salen type ligand) with Cupper(II) Ions in Different Solvents: Spectrophotometric and Conductometric Study. International Journal of New Chemistry 7(1), 1-13.

Fang, G.Z., Liu, Y.W., Meng, S.M. Guo, Y., 2002. Spectrophotometric determination of lead in vegetables with dibromo-p-methyl-carboxysulfonazo. Talanta 57, 1155-1160.

Fat'hi, M.R., Shamsipur, H., 1993. Spectrophotometric Study of Zinc, Cadmium and Lead Complexes with Murexide in Binary Ethanol-Water Mixtures. Spectroscopy Letters 26(9), 1797-1804.

Fowler, B.A., 2009. Monitoring of human populations for early markers of cadmium toxicity: a review. Toxicology and Applied Pharmacology 238, 294-300.

Grudpan, K., Jakmunee, J., Vaneesorn, Y., Watanesk, S., Maung, U. A., Sooksamiti, P., 1998. Flow-injection spectrophotometric determination of calcium using murexide as a color agent. Talanta 46, 1245-1257.

Khan, H., Ahmed, M.J., 2006. A simple spectrophotometric method for the determination of trace level lead in biological samples in the presence of aqueous micellar solutions. Spectroscopy 20, 285–297.

Kong, T., Liu, G.W., Li, X.B., Wang, Z., Zhang, Z.G., Xie, G.H., Zhang, Y., Sun, J., Xu, C., 2010. Synthesis and identification of artificial antigens for cadmium and copper. Food Chemistry 123, 1204-1209.

Kumar, B.N., Kumar, S.H., Redhi, G.G., Jyothi, N.V.V., 2016. Spectrophotometric Determination of Cadmium(II) in Water and Soil Samples Using Schiff's Bases. Asian Journal of Chemistry 28(8), 1861-1866.

Mahesar, S.A., Sherazi, S.T., Niaz, A., Bhanger, M.I., Uddin, S., Rauf, A., 2010. Simultaneous assessment of zinc, cadmium, lead and copper in poultry feeds by differential pulse anodic stripping voltammetry. Food and chemical toxicology 48, 2357-2360.

Masoud, M.S., Kassem, T.S., Shaker, M.A., Ali, A.E., 2006. Studies On Transition Metal Murexide Complexes. Journal of Thermal Analysis and Calorimetry 84(3), 549–555.

Ojeda, C.B., de Torres, A.G., F. Rojas, S., Cano Pavon, J.M., 1987. Fluorimetric determination of trace amounts of gallium in biological tissues. Analyst 112(11), 1499-1501.

Pan J.M., Li Z.J., Zhang Q.Y., Fang G.Z., 2003. New Chromogenic Reagents and Their Application in Spectrophotometry. Chemical Industry Publishing House, Beijing.

Reddy, D.H.K., Seshaiah, K., Reddy, A.V.R., 2011. Synthesis, characterization and biological activity of Cu(II) and Ni(II) complexes of 3-hydroxy- 4(Pyridine-2-yl-methylene amino) benzoic acid. Oriental Journal of Chemistry 27(3), 1141-1147.

Ullah, M.R., Haque, M.E., (2010). Spectrophotometric Determination of Toxic Elements (Cadmium) In Aqueous Media. Journal of Chemical Engineering, IEB 25(1), 1-12.

Yaghi, M.M., Elsherif, K.M., El-Shawish, A.A., 2022. Assessment of some Heavy Metals in Potato and Corn Chips available in Libyan Market. Arabian Journal of Chemical and Environmental Research 9(1), 122–135.

Zaky, M., Amin, A.S., Elgendy, Kh., Gomaa, A., 2017. Direct Spectrophotometric Determination of Lead (II) in Industrial Samples using 1,3-Benzenediamine, N,N'-bis(2-furanylmethylene) in Presence of Surfactant. Bulletin of faculty of Science, Zagazig University. (39), 134-148.

Zhai, Q-Z., Li, J-M., Zhang, J-P., 2013. Spectrophotometric Determination of Lead in Tea Leaf Sample with Dibromo-p-chloro-arsenazo. Asian Journal of Chemistry 25(1), 538-540.

Zhu, Y., Chiba, K., 2012. Determination of cadmium in food samples by ID-ICP-MS with solid phase extraction for eliminating spectral-interferences. Talanta 90, 57-60.

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