INNSPUB

Journal of Biodiversity and Environmental Sciences (JBES)
ISSN: 2220-6663 (Print) 2222-3045 (Online)
Vol. 16, No. 3, p. 56-64, 2020
http://www.innspub.net

RESEARCH PAPER

OPEN ACCESS

A novel green spectrophotometric method for the analysis of Cadmium using Benzohydrazide chelating agent

Muhammad Kashif Channa, Ghulam Abbas Shar*, Gul Afshan Soomro, Muhammad Bachal Korai

Institute of Chemistry, Shah Abdul Latif University, Khairpur, Sindh, Pakistan

Article published on March 30, 2020

Key words: Benzohydrazide (BH), Cadmium, Spectrophotometry, Triton X-100

Abstract

Various methods are present for the analysis at trace level of Cadmium (Cd) metal ions. Most of the methods are time taking, tedious, toxic and sophisticated. Recently some less sensitive and less selective spectrophotometric methods were developed for the determination of Cd (II) ions. We have developed a convenient, rapid, selective and sensitive method for the investigation of Cd (II) at trace level using Benzohydrazide (BH) as chelating agent in surfactant 3.0% Triton X-100 micellar media. Proposed method showed enhancement in the analytical characteristics. The maximum absorbance of complex Cd-BH was measured at ☐ instead of it $_{max}$ 323.9nm at pH 7. The Lambert Beer's law was obeyed over the range of 0.1-5.0 µgmL^{-1} and 1:2 ligand to metal ratio was obtained for complex. The Sandell's sensitivity and molar absorptivity were found to be as 6.2ngcm^{-2} and ε 3.05×10^{4} L mol^{-1}cm^{-1} respectively. Detection limit was found as 6.2ng/mL. The proposed technique was effectively employed for the estimation of Cd (II) ions from various biological, natural, alloys, environmental and industrial samples.

***Corresponding Author:** Ghulam Abbas Shar ✉ gabbas.shar@salu.edu.pk

Introduction

Metals play vital role in daily and biological life. Metals may potentially be vital like cobalt, zinc, nickel, manganese, iron, copper etc and some are toxic such as arsenic, lead, mercury instead of and cadmium etc. (Dogan Uluozlu *et al.*, 2007, Korai MB, 2019). Sometimes the consumption of excessive amounts of essential metals can also have toxic effects on the health of humans (Singh *et al.,* 2011). Cadmium is a highly toxic heavy metal. Cadmium is present in the earth's crust in an amount of approximately 0.1 parts per million (Wedepohl, 1995), is often present in the form of impurities in deposits of lead or zinc and is thus mainly produced in the form of a byproduct of the zinc or lead smelting process. It is hazardous at extremely lower levels of exposure and has both acute and chronic health and environmental effects (World Health Organization, 2003). Cadmium does not degrade nature and therefore remains in circulation when released into the environment (World Health Organization, 2003). This metal is highly poisonous and accounted for numerous fatalities (Key *et al.,* 1977). Smoking is assumed the highest source of human exposure to cadmium (Friberg, 2018). The level of Cd in the blood and kidneys is consistently greater in people who smoke than those who do not (Bernhoft, 2013).

The common symptoms of cadmium toxicity are instant high blood pressure, diarrhea, vomiting, nausea, shortened lifespan, instead of ; damage to the kidneys, pneumonia, growth retardation, dry throat, asphyxia, headache, severe disorders of essential organs and risks of prostate carcinoma (Fergusson, 1989; World Health Organization, 2003). Worst case is the condition known as "ItaiItai" that leads to progressive deterioration of structure of the bones, diminished stature and finally, complete destruction of the whole skeletal system (Venugopal & Luckey, 1979). People who come into contact with cadmium through air, water and foodstuffs are at serious risk to health, including lung, liver and kidney failure (Mezynska & Brzóska, 2018). Therefore, the monitoring of Cd (II) traces in ecological samples is essential. The analysis of cadmium traces has been given high attention in the fight against ecological contamination (Jamaluddin *et al.,* 2014). The cadmium investigation has received a lot of attention in the study of environmental pollution (Korai MA, 2019).

Formerly, several derivatizing reagents like thiosemicarbazone derivatives (Koduru & Lee, 2014; Reddy *et al.,* 2010), aminophenols (Burham N, Abdel-Azeem SM, and El-Shahat, 2011), luminol (Abbasi, Bahiraei & Abbasai, 2011), aminobenzene (Wang *et al.,* 2014), hydroxyquinoline (Aşkun *et al.,* 2008), kerosene (Mohammed, Hussein & Albdiri, 2018), quinoline (Naghibzadeh & Manoochehri, 2018), resorcinol (Sanguthai & Klamtet, 2015) and sulfonic acid (Zhang *et al.,* 2016) have been previously reported for Cd (II) analysis in various environmental matrixes. Several analytical methods for the detection of Cd(II) in natural matrixes have been described so far, like electrochemical methods (Velmurugan & Chen, 2017), UV/Vis spectrophotometry, inductively coupled plasma atomic emission spectroscopy (Wei, Wu & Han, 2015), atomic absorption spectroscopy (Chahid *et al.,* 2014) and voltammetry (Rosolina *et al.,* 2015). These techniques generally involve phases of change and are more costly to be quantified.

Most of the methods are time taking, tedious, toxic and sophisticated. Novel procedures are required to analyze the cadmium ions at trace level. The technique of spectrophotometry is very popular for its easiness, accuracy, rapidity and economic cost of instrument. Cd (II) ions are determined using chelating agents in UV-Vis spectrometry.

In spectrophotometric study of Cd (II), the metal reacts with the derivatizing agent to form a metal complex that is insoluble and then dissolves by solvent-extraction process. Several procedures for spectrophotometric estimation for cadmium have been developed to substitute the previous method of solvent extraction by the use of micellar system (surfactants) (Korai MB *et al.,* 2019; Soomro and Shar, 2014; Yun and Choi, 2000). Micellar methods showed enhancement in the analytical characteristics of method for the analysis of Cd (II) ions in solubilizing the complex (Olkowska and Polkowska, 2012). Recently some less sensitive and less selective spectrophotometric methods were developed for the determination of Cd(II) ions. We have developed a convenient, rapid, selective and sensitive method for the investigation of Cd (II) at trace level using Benzohydrazide (BH) as chelating agent in surfactant 3.0% Triton X-100 micellar media. Proposed method showed enhancement in the analytical characteristics. The proposed technique has been effectively employed for the estimation of Cd (II) ions from various biological, natural, alloys, environmental and industrial samples.

Material and method

UV-Vis Cecil CE 9500 spectrophotometer having quartz cells with path length of 10 mm. Atomic absorption spectrometer (Analyst-800 Perkin Elmer) model. IR spectrometer (Hitachi). pH/conductivity meter (Sension156 HACH Company USA) model.

Preparation of Reagents

The 1000μg/L stock solution of cadmium (II) ion was prepared in double distilled water from high purity salts supplied by (Merck, Darmstadt, Germany). Further metal ion solutions were also made by dissolving salts to analyze the interferences of ions (Korai MA *et al.*, 2019).

The 4×10^{-4}M solution of BH was prepared by taking its 0.0544g in least quantity of ethanol in 1000mL flagon and added 3.0% Triton X-100 up to mark. Triton X-100 3.0% solution was made by taking its 3g in 100mL calibrated flagon and the volume was made with distilled H_2O. Buffers of pH 1 to 10 were made according methods (Perrin, 2012), by mixing appropriate volumes of KCl (0.2 M)-HCl (0.2M) of both for pH 1.0 to 4.0, CH_3COOH (0.2 M)-CH_3COONa (0.2 M) volumes for solution of pH 5.0 to 6.0, KH_2PO_4 (0.1 M)-NaOH (0.1 M) volumes for solution of pH 6.5 to 8.0 and $Na_2B_4O_7$ (0.025 M)-HCl (0.1 M) volumes for preparation of the solution of pH 9.0 to 10.0. All the chemicals were used of analytical grade with high purity (Merck/Fluka).

General method for determination of cadmium (II) ions

The solution of the cadmium(II) ions with varying concentration 0.06 to 10μgmL^{-1}, 2mL of reagent Benzohydrazide (BH) solution, 2mL of pH 7 buffer solution and 2mL of 3.0% Triton X-100 were mixed in 10mL measuring flagon. The solution was well shaken and deionized H_2O was mixed up to the end. The absorbance of Cd (II)-BH complex was recorded at λ_{max} 323.9nm against BH as blank.

Cadmium (II) ions analysis from steel

Certified reference materials such as GBW07301a (sediment) and BCR NO.151 (milk powder) were taken, digested and the volume was made. The sample solutions were transferred into measuring flagon, mixed the Benzohydrazide (BH), pH 7 buffer 2mL, and 3.0% Triton X-100 2mL for formation of complex. The absorbances were measured. Results are presented in Table 3.

Investigation of Cadmium (II) ions in waste water sample

2L waste water was collected from village Sohu Kanasara district Khairpur, Pakistan. The sample was filtered and mixed concentrated nitric acid of 4mL volume and hydrogen peroxide 2mL volume for the digestion (Iqbal *et al.*, 2017). Then it was heated at about 110°C in oven for the preconcentration and the volume of 25mL was made. Finally the sample was taken in volumetric flask, added Benzohydrazide (BH) 2mL, pH 7 buffer 2mL, and 3.0% Triton X-100 2mL (Krishna *et al.,* 2010). The absorbance for Cd-BH complex was measured. Outcomes are displayed in table 4.

Investigation of Cadmium (II) ions in tap watersample

The sample of tap water of 1000mL volume was collected from village Naroo Dhoro district Khairpur, Pakistan and heated in oven for preconcentration, filtered, mixed concentrated nitric acid of 2mL volume to it. Finally the sample was transferred in calibrated bottle, mixed Benzohydrazide (BH) 2mL, pH 7 buffer 2mL, and 2mL of 3.0% Triton X-100 (Korai MA *et al.,* 2019). The complex absorbance was obtained. Outcomes are shown in Table 5.

Investigation of Cadmium (II) ions in biological certified materials

250mL of different kinds of biological certified materials were added in 10mL of H_2SO_4 20% and 10mL of HNO_3 conc. All samples were boiled and diluting with deionized H_2O. Then they were filtered and neutralized. Finally solutions were transferred in calibrated flagon, mixed Benzohydrazide (BH) 2mL, pH 7 buffer 2mL, and 2mL of 3.0% Triton X-100 and solution of tartarate 2mL (Jamaluddin *et al.,* 2014). Absorbances of complexes were measured. Outcomes are presented in table 6**.**

Analysis of Cadmium (II) in natural matrices

Natural matrices like 4g of hairs, 15mL of urine and 3mL of blood were added in 10mL of H_2SO_4 20% and 10mL of HNO_3 conc., and H_2O_2 2mL volume for digestion. All samples were boiled and diluting with deionized H_2O. Then they were filtered and neutralized (Jamaluddin *et al.,* 2014). Finally solutions were transferred in calibrated flagon, mixed Benzohydrazide (BH) 2mL, pH 7 buffer 2mL, solution of tartarate 2mL and 2mL of 3.0% Triton X-100. Absorbances of complexes were measured. Outcomes are presented in table 7.

Results and discussion

Cd (II) ion reaction with Benzohydrazide (BH) showed transition due to electronic charge transfer. Benzohydrazide contributes pairs of electrons from oxygen of carbonyl (C=O) and nitrogen of amino (NH_2) groups. The proposed structure of Benzohydrazide with Cd (II) ions are given in Fig. 1 (Koksharova *et al.,* 2018). Benzohydrazide presented bands of absorption as a result of transitions ($n \rightarrow \pi^*$) of BH to BH transformation of charge (LLCT) from nitrogen of amino (NH_2) group and oxygen atom of carbonyl (C=O) at λ_{max} 285.2nm in micellar 3.0% Triton X-100 is given in Fig. 2. Spectrum of cadmium (II)- Benzohydrazide showed absorption peaks as a result of ($n \rightarrow \pi^*$) transition from Benzohydrazide to Cd (LMCT) at λ_{max} 323.9 nm for $-NH_2$ and C=O- as shown in Fig. 3. The Cd (II)-complex showed the constant maximum absorbance and was stable up to 120 minutes.

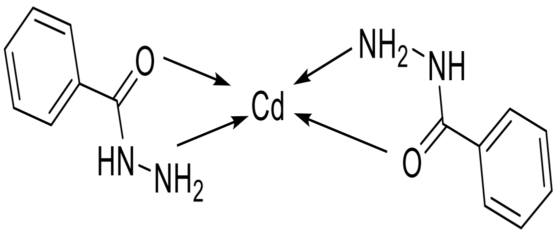

Fig. 1. Proposed structure for bis[benzohydrazide]-cadmium (II) complex.

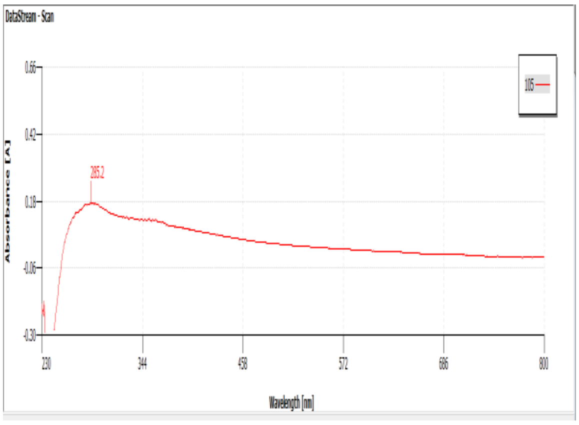

Fig. 2. UV-Vis spectra of BH at (λ_{max}285.2nm) in 3.0% Triton X-100.

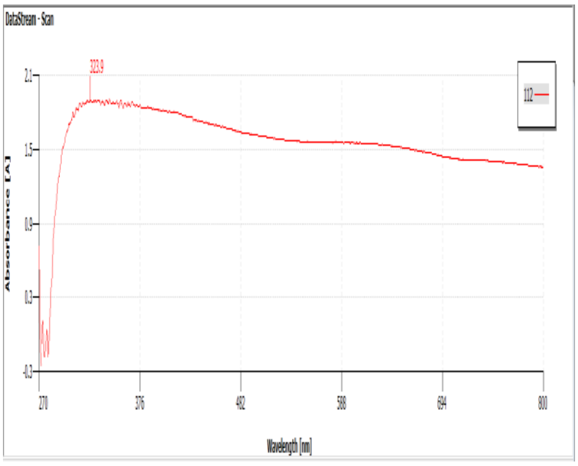

Fig. 3. UV-Vis spectrum of cadmium (II)-$(BH)_2$ complex at (λ_{max} 323.9 nm) in Triton X-100.

Stoichiometric molar ratio was found by Job's method for Cd (II) and Benzohydrazide ration (Malik & Rao, 2000). Cadmium (II) complex showed absorbance plots versus Cd (II) to Benzohydrazide equimolar mole fraction 1:2 for cadmium (II)-Benzohydrazide is shown in Fig. 4. Effect of Benzohydrazide concentration on Cd(II)-BH complex absorbance was measured by varying 0.5 to 10.0×10-

^{4}M concentration of Benzohydrazide; which Cd(II) ions 1.0mM were kept constant. It was observed that when Cd (II) 1.0mM concentration; while Benzohydrazide molar ratios was ranging 4.0×10^{-4}M for constant maximum absorbance. The concentration of BH was optimized on constant concentration of Cd (1m.mole) is shown in Fig. 5. In 10mL calibrated flagon mixed 2mL of Cd(II) ions, 2mL of 4.0×10^{-4}M Benzohydrazide buffer pH 7, and 2mL of 3.0% triton X-100 for complexation. The 3.0% triton X-100 surfactant was also optimized and employed it during study, and its value is greater than critical micellar value. Optimal pH selectivity for constant maximum absorption was found at pH 7, employed during study and is shown in Fig. 6.

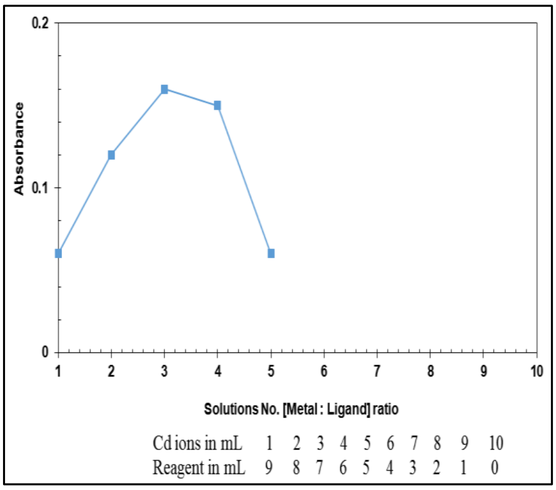

Fig. 4. Cd(II)-BH complexes composition by the Job's method.

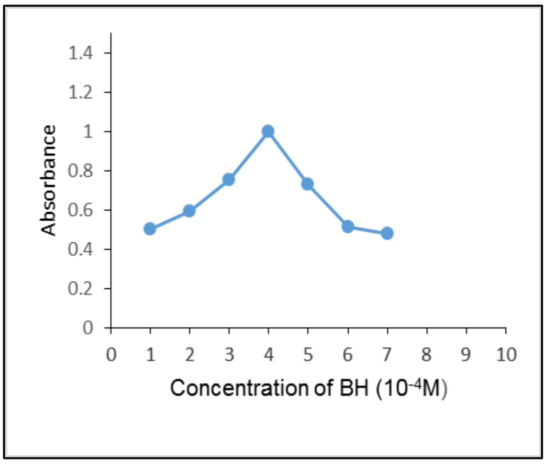

Fig. 5. BH concentration effect on cadmium (II)-BH complex.

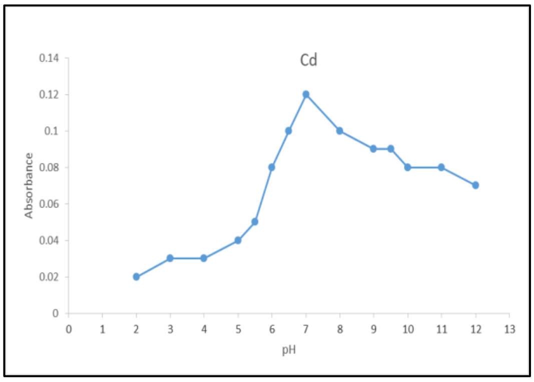

Fig. 6. Effect of pH on absorbance of Cd (II)-BH complex.

Calibration curve was obtained over the range 0.1-5.0µg/mL at λ_{max} 323.9 nm with correlation coefficients R^2 value 0.9996 is shown in Fig. 7. Coefficient of molar absorptivity was found 3.05×10^{4}mol^{-1}cm^{-1} at λ_{max} 323.9nm is given in Table 1. The value for Sandell's sensitivity was found 6.2ngcm^{-2} is shown in Table 1. The limits of detection was found 6.2ngmL^{-1} is shown in Table 1. Proposed method showed improvement in selectivity and sensitivity than reported extraction methods as shown in table 8.

Table 1. Optimized parameters of Cd-BH complex.

Parameters	Cadmium
Beer's Law range µgmL^{-1}	0.1-5.0
Absorption max: λ_{max}	323.9 nm
Molar absorptivity mol^{-1} cm^{-1}	3.05×10^{4}
pH	7
Triton x-100 3.0%	2.0mL
BH	4.0×10^{-4} mol^{-1}L^{-1}
M : L Ratio	1 : 2
Sandell's sensitivity	6.2 ngcm^{-2}
D.L	6.2 ng/mL
(R^2)	0.9996

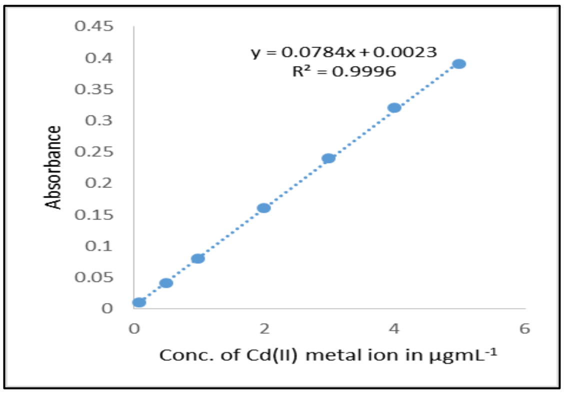

Fig. 7. Calibration graph of Cd (II)-BH complex.

In the formation of the metal complex, the interferences of different cations and anions were studied. $KClO_3$, KSCN and sodium tartrate interfered to a lesser extent and displayed more than 800µgmL^{-1} found interferences in the absorption of cadmium (II) complexes at their trace levels. EDTA, dimethylglycine and ascorbic acid were utilized as masking agents to reduce foreign ion interference (Usha & Rajini, 2012; Taher, 2003) are shown in Table 2.

Table 2. Foreign ions effect on the Cd(II)-BH complex µgmL^{-1}.

Ions/ salts	Cadmium
Na_2 tartarate, KSCN, $KClO_3$	800
Zn(II)	100
Al(III)	100
Mn(III)	10
Na_2 citrate	800
Pb(II)	3
$Na_2C_2O_4$	200
Cd(II)	-
Cr(VI)	8
KCN	30
Mg(II)	600
V(III)	100
Mn(II)	500
Cr(III)	80
Cd(II)	2

Validation of method

Proposed method's results were validated with AAS, Biological certified reference materials, % age recovery test at 95% confidence interval. Certified reference materials and tap water have been evaluated for accuracy and reliability of technique; the outcomes are given in Table 3-6.

Table 3. Investigation of cadmium(II) in certified reference materials.

Sample	Metal ion	Certified value (ng g^{-1})	proposed method (ng g^{-1})	%RSD	AAS method (ng g^{-1})	RSD%	Recovery
GBW07301a (sediment)	Cd(II)	110 ± 3	107 ± 6	0.3	108 ± 5	0.2	97.27
BCR NO.151 (milk powder)	Cd(II)	101 ± 8	99 ± 9	0.7	100 ± 7	0.3	98.01

Table 4. Determination of cadmium from waste water sample.

Sample	Metal ion	Metal (µg) present	Metal (µg) found	RSD%	Relative error%	Recovery%
Industrial waste water	Cd(II)	4.5	4.3	0.9	0.2	95.5

Table 5.% age recovery of cadmium added in water samples.

Analyte ions	Added content (µgmL^{-1})	Found (µgmL^{-1})	R (%)
Cd(II)	3.00	2.95	98.3

Table 6. Determination of cadmium in certified biological samples.

Samples	Certified value of Cadmium (µgg^{-1})	Found Cadmium (µg g^{-1})
BCR 397 (human hair)	0.521 ± 0.024	0.513 ± 0.032
BCR 186 (pig kidney)	2.71 ± 0.15	2.70 ± 0.16

Table 7. Analysis of cadmium in human hair and fluids.

Sources of the Samples	Samples	Cadmium (µgL^{-1})			
		AAS		Proposed method	
		Found	RSD (%)	Found	RSD (%)
Kidney disease patient	Blood	220.5	0.3	220.3	0.4
	Urine	56.8	0.5	56.7	0.3
Hypertension patient	Blood	98.3	0.8	98.1	0.6
	Urine	30.6	0.9	30.5	0.7
Human Hair	Hairs	60.3	0.7	60.1	0.6

Table 8. Comparison of cadmium investigation using Benzohydrazide.

Metals	Procedures	References
Cd(II)	in Tween 80, D.L. 0.039 µgmL^{-1}	Yun & Choi, 2000
Cd(II)	in Triton X-100, ε 2.05×10^4 mol^{-1}cm^{-1}, λ_{max} 425nm, D.L 0.02 µgmL^{-1}	H. Abdollahi *et al.*
Cd(II)	in 3.0% Triton X-100, ε 3.05×10^4 mol^{-1}cm^{-1}, λ_{max}323.9 nm, D.L. 6.2 ng/mL	Proposed present method

Conclusion

The present method is simple, rapid, sensitive, selective, reproducible, non-extractive, and versatile spectrophotometric method for determination of cadmium (II) ions at trace level.

The proposed method is environment friendly, showed higher selectivity and sensitivity and has substituted the old solvent extraction methods that was time taking, expensive and venomous.

The results showed good improvement in sensitivity, molar absorption than reported methods as shown in table 8. The proposed technique was effectively employed for the estimation of Cd (II) ions from various biological, natural, alloys, environmental and industrial samples.

References

Abbasi S, Bahiraei A, Abbasai F. 2011. A highly sensitive method for simultaneous determination of ultra trace levels of copper and cadmium in food and water samples with luminol as a chelating agent by adsorptive stripping voltammetry. Food chemistry **129(3),** 1274-1280.

Aşkun H, Gülbakan B, Çelikbıçak Ö, Uzun C, Güven O, Salih B. 2008. Preconcentration and matrix elimination for the determination of Pb (II), Cd (II), Ni (II), and Co (II) by 8-hydroxyquinoline anchored poly (styrene-divinylbenzene) microbeads. Journal of applied polymer science **107(4),** 2714-2722.

Bernhoft RA. 2013. Cadmium toxicity and treatment. The Scientific World Journal **2013,** 1-7.

Burham N, Abdel-Azeem SM, El-Shahat MF. 2011. Determination of heavy metal ions in environmental samples employing preconcentration on novel resins of polyurethane foam linked with o-Aminophenol or o-Hydroxyphenylazonaphthol. International Journal of Environmental and Analytical Chemistry **91(3),** 197-212.

Chahid A, Hilali M, Benlhachimi A, Bouzid T. 2014. Contents of cadmium, mercury and lead in fish from the Atlantic sea (Morocco) determined by atomic absorption spectrometry. Food chemistry **147,** 357-360.

Dogan Uluozlu O, Tuzen M, Mendil D, Soylak M. 2007. Trace metal content in nine species of fish from the Black and Aegean Seas, Turkey. Food Chemistry **104,** 835-840.

Fergusson JE. 1989. The toxicity of heavy elements to human beings in: The Heavy Elements: Chemistry, Environmental Impact and Health Effects. Pergamon Press, Oxford 548.

Friberg L. 2018. Cadmium in the Environment. CRC press.

Iqbal HH, Shahid N, Qadir A, Ahmad SR, Sarwar S, Ashraf MR, Arshad HM, Masood N. 2017. Hydrological and Ichthyological Impact Assessment of Rasul Barrage, River Jhelum, Pakistan. Polish Journal of Environmental Studies **26(1),** 107-114.

Jamaluddin MA, Zannat T, Fatema Z. 2014. A Simple Spectrophotometric Method for the Determination of Trace Level of Cadmium in Real, Environmental, Biological, Tobacco, Fertilizer and Soil Samples Using 2', 3, 4', 5, 7 Pentahydroxyflavone. American Chemical Science Journal **4(4),** 481-503.

Key MM, Henschel AF, Butter J, Ligo RN, Tabershaed IR. 1977. Occupational Diseases-A Guide to Their Recognition, U. S. Department of Health, Education and Welfare, US Government Printing, Washington, DC 265.

Koduru JR, Lee KD. 2014. Evaluation of thiosemicarbazone derivative as chelating agent for the simultaneous removal and trace determination of Cd (II) and Pb (II) in food and water samples. Food chemistry **150,** 1-8.

Koksharova TV, Mandzii TV, Stoyanova IV. 2018. Coordination Compounds of Cobalt (II), Nickel (II), and Zinc (II) Malonates and Phthalates with Benzohydrazide. Russian Journal of General Chemistry **88(3),** 500-504.

Korai MA, Shar GA, Soomro GA, Korai MB. 2019. Environmental friendly spectrophotometric method for the determination of cadmium (II) using 1-nitroso-2-naphthol in micellar media. Journal of Biodiversity and Environmental Sciences **15(4),** 1-9.

Korai MA. 2019. Method development for spectrophotometer determination of chromium, manganese, vanadium and cadmium complexing with 1-nitroso-2-naphthol. PhD. Thesis, Shah Abdul Latif University Khairpur, Sindh, Pakistan.

Korai MB, Shar GA, Soomro GA, Shar NA, Shar RA. 2019. Eco-friendly method for the estimation of cobalt (II) in real samples using 1-(2-Thiazolylazo)-2-naphthol. Journal of Biodiversity and Environmental Sciences **15(1),** 12-21.

Korai MB. 2019. Spectrophotometer Determination of cobalt, nickel, iron, copper and zinc using 1-(2-Thiazolylazo)-2-Naphthol in Micellar Media. PhD. Thesis, Shah Abdul Latif University Khairpur, Sindh, Pakistan.

Krishna GD, Devanna N, Chandrasekhar BK. 2010. Direct and derivative spectrophotometric determination of cadmium(II) in presence of micellar medium in biological materials and in alloy samples using cinnamaldehyde-4-hydroxy benzoylhydrazone (CMHBH). International Journal of Pharma and Biosciences **1(3),** 1-19.

Malik AK, Rao ALJ. 2000. Spectrophotometric determination of cobalt, nickel, palladium, copper, ruthenium and molybdenum after extraction of their isoamyl xanthate complexes into molten naphthalene. Journal of Analytical Chemistry **55(8),** 746-749.

Mezynska M, Brzóska MM. 2018. Environmental exposure to cadmium - A risk for health of the general population in industrialized countries and preventive strategies. Environmental Science and Pollution Research **25(4),** 3211-3232.

Mohammed AA, Hussein MA, Albdiri AD. 2018. Application of bulk liquid membrane technique for cadmium extraction from aqueous solution. Arabian Journal for Science and Engineering **43(11),** 5851-5858.

Naghibzadeh L, Manoochehri M. 2018. Determination of nickel and cadmium in fish, canned tuna, black tea, and human urine samples after extraction by a novel quinoline thioacetamide functionalized magnetite/graphene oxide nanocomposite. Carbon Letters (Carbon Lett.) **26,** 43-50.

Olkowska E, Polkowska Z, Namiesnik J. 2012. Analytical procedures for the determination of surfactants in environmental samples. Talanta **88(2012),** 1-13.

Perrin DD. 2012. Buffers for pH and Metal ion Control: Springer science & business media.

Reddy SA, Reddy KJ, Reddy AV. 2010. Analytical Applications of 2, 6-Diacetylpyridine-bis-4-phenyl-3-thiosemicarbazone (2, 6-DAPBPTSC): Determination of Cd (II) in Foods and Water Samples. Journal of the Chinese Chemical Society **57(2),** 236-243.

Rosolina SM, Chambers JQ, Lee CW, Xue ZL. 2015. Direct determination of cadmium and lead in pharmaceutical ingredients using anodic stripping voltammetry in aqueous and DMSO/water solutions. Analytica chimica acta **893,** 25-33.

Sanguthai S, Klamtet J. 2015. Preconcentration and Determination of Cadmium in Natural Water using Amberlite XAD-4/4-(2-Pyridylazo) Resorcinol Resin Prior to Flame Atomic Absorption Spectrometric Detection. Naresuan University Journal: Science and Technology (NUJST) **23(2),** 8-20.

Singh R, Gautam N, Mishra A, Gupta R. 2011. Heavy metals and living systems: An overview. Indian Journal of Pharmacology **43(3),** 246-253.

Soomro GA, Shar GA. 2014. A Simple Spectrophotometric Method for determination of cadmium (II) using 1-(2- pyridylazo)-2-naphthol in micellar aqueous solution of CTAB. Ultra Chemistry **10(2),** 95-104.

Taher MA. 2003. Flame Atomic Absorption Spectrometric Determination of Trace Cadmium in Alloys and Biological Samples after Solid-Liquid Extraction and Preconcentration with Use of Nitroso-S. Microchimica Acta **141,** 101-106.

Usha G, Rajni R. 2012. Simultaneous determination of Zinc (II) and Cobalt(II) by first order derivative spectrophotometry in Triton X-100 micellar media. Research Journal of Chemical Science **2(11),** 8-13.

Velmurugan M, Chen SM. 2017. Synthesis and characterization of porous MnCo2 O4 for electrochemical determination of cadmium ions in water samples. Scientific reports **7(1),** 1-8.

Venugopal B, Luckey TD. 1979. Metal Toxicity in Mammals-2, Plemum Press, New York 76.

Wang Z, Wang H, Zhang Z, Yang X, Liu G. 2014. Sensitive electrochemical determination of trace cadmium on a stannum film/poly (p-aminobenzene sulfonic acid)/electrochemically reduced graphene composite modified electrode. Electrochimica Acta **120,** 140-146.

Wedepohl KH. 1995. The composition of the continental crust. Geochimica et cosmochimica Acta **59(7),** 1217-1232.

Wei XS, Wu YW, Han LJ. 2015. Determination of lead and cadmium in water and pharmaceutical products by inductively coupled plasma optical emission spectrometry with preconcentration by thiourea immobilized silica. Analytical Letters **48(6),** 996-1008.

World Health Organization (WHO). 2003. Nordic Council of Ministers, cadmium review.

Yun J, Choi H. 2000. Micellar colorimetric determination of iron, cobalt, nickel and copper using 1-nitroso-2-naphthol. Talanta **52,** 893-902.

Zhang Y, Mao X, Liu J, Wang M, Qian Y, Gao C, Qi Y. 2016. Direct determination of cadmium in foods by solid sampling electrothermal vaporization inductively coupled plasma mass spectrometry using a tungsten coil trap. Spectrochimica Acta Part B: Atomic Spectroscopy **118,** 119-126.