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Environmental friendly spectrophotometric method for the determination of cadmium (II) using 1-nitroso-2-naphthol in micellar media

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Abstract

Metals play vital role in living and environmental systems. Some metals are essential and others are toxic for biological system. Manganese, iron, copper and cobalt are essential, while arsenic, lead and cadmium are toxic. Essential elements can show toxic effect, when their concentration is above certain level; so their monitoring is necessary for their role. The research purpose was to establish rapid, convenient, sensitive, and reproducible spectrophotometric method for the detection of Cd (II) ions at trace level using NNPh reagent in 1.0% SDS micellar media and replaced the old solvent extraction method, which was time consuming, costly and use of toxic solvents. The proposed method is simple, rapid and environmental friendly. Stoichiometric metal to ligand ratio was found 1:2 for the Cd-[NNPh]₂ formation. The coefficient molar absorption (ϵ) was found $1.02 \times 10^4 \text{ Lmol}^{-1} \text{ cm}^{-1}$ at λ_{max} 579.9nm. Linear calibration curve was obtained over the concentration range $0.5\text{-}4.0 \mu\text{g mL}^{-1}$. The proposed method was applied for the investigation of Cd(II) from different alloys, biological, environmental and pharmaceutical samples.

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Introduction

Metal have important role in environmental and biological systems. Many metal ions such as zinc (II), vanadium (III), chromium (III) and manganese (II) are essential for human and other living organisms. While other metals like As, Cd, Pb and Hg are toxic to living beings at certain concentration levels (Ensafi and Shiraz 2008; Hedberg *et al.*, 2011). Even essential metals are toxic at above certain concentration level (Delavar *et al.*, 2017). Cadmium (II) is a toxic and environmental pollutant. The determination of trace amounts of cadmium has received very much attention in the battle against environmental pollution (Jamaluddin *et al.*, 2014). The smokers inhale the 10 percentage of cadmium from the whole quantity in the cigarettes. The excessive intake of cadmium may cause high blood pressure in humans (Tokalioglu *et al.*, 2007). The greater content of cadmium was detected in nephron and urine of the patients of high blood pressure. The investigation of cadmium has gotten a great attention in the ecological contamination study (Korai, MA, 2019).

Various methods are present for investigation of Cd (II) ions such as UV/V is spectrophotometry, AAS absorption, colorimetry, emission spectrometry etc (Shanthalakshmi and Belagali, 2009; Ullah and Enamul, 2010; Nosier, 2003; Tokalioglu *et al.*, 2009; Naeemullah, *et al.*, 2013). Many of the given methods are costly because of the high price of tools, time-consuming and tedious. New methods are required to determine the cadmium ions at trace level. The spectrophotometric technique is much prevalent because of its simplicity, precision, speed and inexpensive instrument price. Cd (II) ions are determined using chelating agents in UV-Vis spectrometry. In spectrophotometric study of Cd (II), the metal is reacted with complexing reagent and insoluble metal complex is formed then is solubilized with solvent extraction. Various methods for spectrophotometric determination for cadmium have been developed to substitute the previous method of solvent extraction by the use of micellar system (surfactants) (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 1-nitroso-2-naphthol as chelating agent in surfactant 1.0% SDS micellar media. The world method was successfully applied for the determination of Cd (II) ions from various biological and environmental samples.

Material and method

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

Preparation of Reagents

The cadmium (II) ion stock solution (1000 μ g/L) was prepared in double distilled water from high purity salts supplied by (Merck, Darmstadt, Germany). Other solutions of metal ions were also prepared from their salts for studying the effect of interfering analytes (Korai, MA, 2019). The solution of NNPh was made by adding its 75mg in 50mL flask and dissolving in minimum amount of ethyl alcohol and made the volume with 1.0% SDS up to mark (Shar and Soomro, 2006). SDS 1.0% solution was made when 1.00g of SDS was taken in 100mL volumetric flask and made up the volume with distilled water up to the mark. Buffers of pH 1 to 10 were made according methods (Perrin, 2012), by mixing appropriate volumes of KCl (0.2M)-HCl (0.2M) of both for pH 1.0 to 4.0, CH₃COOH (0.2M)-CH₃COONa (0.2M) volumes for solution of pH 5.0 to 6.0, KH₂PO₄ (0.1M)-NaOH (0.1M) volumes for solution of pH 6.5 to 8.0 and sodium borate (0.025M)-HCl (0.1M) 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 different concentrations 0.06-10 μ g/mL, NNPh solution

185ppm (185 μ g/mL), 2mL of pH 8 buffer solution and 2mL of 1.0% SDS solution were mixed in 10mL calibrated flask. The solution was shaken well and D.D water was added up to the mark. The absorbance of Cd (II)-NNPh complex was recorded at λ_{\max} 579.9nm against NNPh as blank (Korai, MA, 2019).

Cadmium (II) ions analysis from steel

1.0g of 651-7 stainless steel was taken in 250mL beaker, added 15mL conc. HNO₃ and added 25mL deionized water. The sample solution was taken in volumetric flask, added the NNPH 185ppm solution, 2mL pH 8 buffer solution and 2mL of 1.0% SDS for complex formation. The absorbance was measured. The results are given in table 3.

Cadmium (II) ions determination from waste water

2L waste water was collected from Sukkur city. This solution was filtered and digested with 4mL of conc. HNO₃ and 2mL of H₂O₂ (Iqbal *et al.*, 2017). The samples were preconcentrated in oven at 110°C and final volume was made 25mL. The liquid sample was transferred in volumetric flask, mixed 2mL of 185ppm NNPh, added 2mL buffer pH 8, and 2mL of 1.0% SDS (Krishna *et al.*, 2010). The complex absorbance was measured. Results are given in table 4.

Cadmium (II) ions investigation from tap water

1000mL tap water solution was collected from Ghotki city and was pre concentrated in oven, filtered, added 2mL of conc. HNO₃. Sample solution was taken in volumetric flask, added 2mL of 185ppm solution of NNPh, added 2mL of buffer pH 8, and 2mL of 1.0% SDS. (Korai, MA, 2019). The absorbance of complex was measured. The results are given in table 5.

Cadmium (II) ions investigation in reference material

50mL of reference materials of various types were digested in 10mL of concentrated HNO₃, 10mL of 20% H₂SO₄. The samples were evaporated and diluted with demonized water. The samples were filtered and neutralized. The sample solutions were taken in volumetric flask, added 2mL NNPh of 185ppm, added 2mL buffer pH8, 2mL of 1.0% SDS and 2mL tartarate solution (Jamaluddin *et al.*, 2014). The complex absorbance was noted. The results are shown in table 6.

Cadmium (II) ions investigation in biological samples

Human blood 3mL, urine 15mL and hair 4g samples were digested with 10mL of conc. HNO₃ and 10mL of 20% H₂SO₄, 2mL of H₂O₂. The samples were evaporated on hot plate and reduced to dryness; residues were diluted, filtered and neutralized (Jamaluddin *et al.*, 2014). The samples were taken in volumetric flask added 2mL of 185ppm NNPh, 2mL buffer pH8, 2mL of 1.0% SDS and 2mL of tartarate (Korai, MA, 2019). The complexes absorbance was measured. The results are shown in table 7.

Cadmium (II) ions investigation in tobacco

5g tobacco and 5g cigarettes of various brands were digested in 10mL of conc. HNO₃, 10mL of 20% H₂SO₄ and 2mL of H₂O₂ (Jamaluddin *et al.*, 2014). The samples were evaporated to reduce to dryness. The residues were dissolved with H₂SO₄, diluted with deionized water and neutralized with NaOH. The samples were taken in volumetric flask added 2mL of 185ppm NNPh, 2mL buffer pH 8, 2mL of 1.0% SDS and 2mL of tartrate. The complexes absorbance was measured. The data is given in table 8.

Cadmium (II) ions investigation in fertilizer

5g of fertilizer of various brands ground finely digested in 10mL concentrated HNO₃; 10mL of 2% of H₂SO₄ and 2mL of H₂O₂. The solutions were evaporated and reduced to dryness. The residues were dissolved with H₂SO₄ 1:90 ratio; diluted, neutralized and filtered with NaOH. The samples were taken in volumetric flask, added 2mL NNPh of 185ppm, 2mL buffer pH8, 2mL of 1.0% SDS, 2mL of EDTA and 2mL of tartrate for complexation. The absorbances were recorded. The data is shown in table 8.

Results and discussion

Cd(II) ion reaction with 1-nitroso-2-naphthol showed transition due to electronic charge transfer. NNPh donates electron pairs from oxygen atom of OH and nitrogen of NO group (Tugsuz and Sevin, 2006). The bonding sites atoms of NNPh structure with Cd (II) ions are given in Fig. 1. NNPh showed absorption bands due to (n \rightarrow π^*) transitions of NNPh to NNPh charge transfer (LLCT) nitro group of nitrogen atom and -OH group at λ_{\max} 377.0 nm in micellar 1.0% SDS

is given in Fig. 2. Spectrum of cadmium (II)-1-nitroso-2-naphthol showed absorption peaks due to transition ($n \rightarrow \pi^*$) from NNPh to cadmium (LMCT) at λ_{max} 579.9 nm for O-N and HO- as shown in Fig. 3. The Cd (II)-complex showed the constant maximum absorbance and was stable up to 120 minutes.

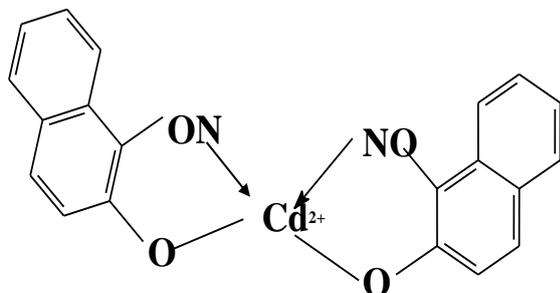


Fig. 1. Structure for bis[1-nitroso-2-naphthol]-cadmium (II) complex.

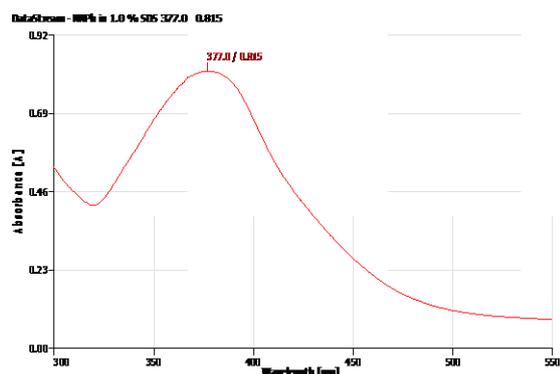


Fig. 2. UV-Vis spectra of NNPh at (λ_{max} 377.0 nm) in 1.0% SDS.

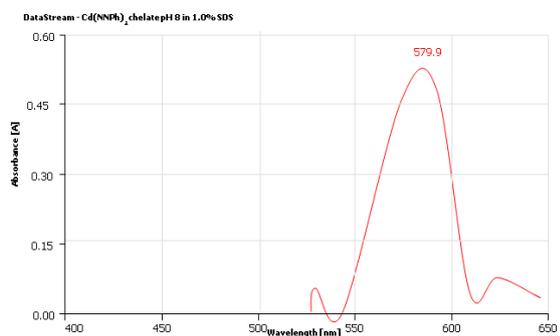


Fig. 3. UV-Vis spectrum of cadmium(II)-(NNPh)₂ complex at (λ_{max} 579.9 nm) in SDS.

Stoichiometric molar ratio was obtained by Job's method of continuous variation Cd (II) and NNPh ratio (Malik & Rao, 2000). Cadmium (II) complex

showed absorbance plots versus Cd (II) to NNPh equimolar mole fraction 1:2 for cadmium (II)-NNPh is shown in Fig. 4 (Korai, MA, 2019). Effect NNPh concentration on Cd (II)-NNPh complex absorbance was measured by varying 5-80mM concentration of NNPh; Cd(II) ions 1.0mM were kept constant. It was observed when Cd (II) 1.0mM concentration; while NNPh molar ratios was ranging 40-70Mm for constant maximum absorbance. The NNPh concentration was optimized at fixed different concentration of Cd (1m.mole) is shown in Fig. 5. In 10mL volumetric flask added 2 gmL⁻¹ of Cd(II) ions, 2mL of 185ppm NNPh buffer pH 8, and 2mL of 1.0% SDS for complexation. The 1.0% SDS surfactant was optimized and this concentration was kept constant throughout study, this value is above the cmc value $8.3 \times 10^{-3}M$. In selectivity of optimum pH for the maximum constant absorbance was observed at pH 8 in the whole studies were kept constant is given in Fig. 6.

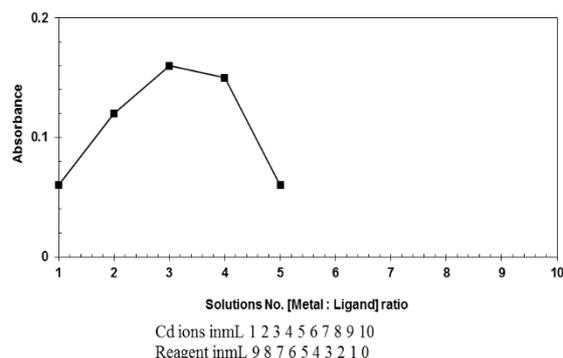


Fig. 4. Cd(II)-NNPh complexes composition by the Job's method.

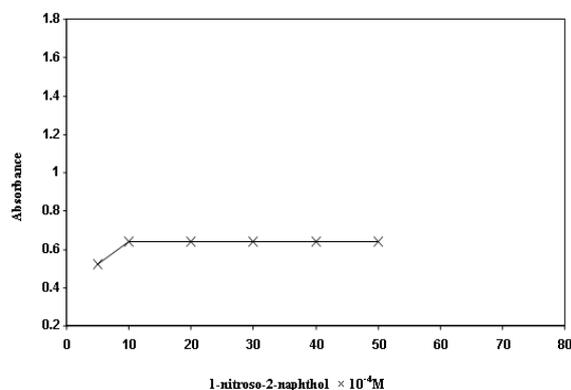


Fig. 5. NNPh concentration effect on cadmium (II)-NNPh complex.

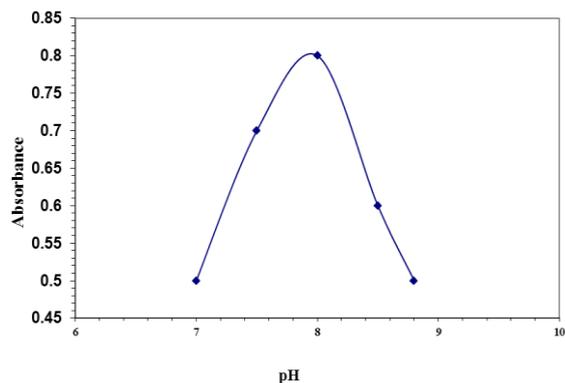


Fig. 6. Effect of pH on absorbance of Cd (II)-NNPh complex.

Calibration curve was obtained over the range 0.5-4.0 $\mu\text{g mL}^{-1}$ at λ_{max} 579.9nm with correlation coefficients R^2 value 0.999 is shown in Fig. 7. The molar absorption coefficient was found $1.02 \times 10^4 \text{ mol}^{-1} \text{ cm}^{-1}$ at λ_{max} 579.9nm is given in Table 1. The value for Sandell's sensitivity was found 5.8 ng cm^{-2} is shown in Table 1. The limits of detection were found 5.8 ng mL^{-1} is shown in Table 1. Proposed method showed improvement in selectivity and sensitivity than reported extraction methods as shown in table 9.

Table 1. Optimized parameters of Cadmium-NNPh complex.

Parameters	Cadmium
Beer's Law range $\mu\text{g mL}^{-1}$	0.5-5.0
Absorption max: λ_{max}	579.9 nm
Molar absorptivity $\text{mol}^{-1} \text{ cm}^{-1}$	1.02×10^4
pH	8
SDS 1.0%	2.0mL
NNPh	$5.0 \times 10^{-4} \text{ mol}^{-1} \text{ L}^{-1}$
M : L Ratio	1 : 2
S.S	5.8 ng cm^{-2}
D.L	5.8 ng/mL
(R^2)	0.999

In metal-chelate formation interference of various cations and anions were investigated. KSCN, sodium tartarate and KClO_3 interfered less and showed beyond $800 \mu\text{g mL}^{-1}$ present confirmed interference in complexes absorbance for cadmium (II) at their minute level. Ascorbic acid and EDTA, dimethyl glycine were used as masking agents to decrease interference of foreign ions (Usha & Rajini, 2012; Taher, 2003) are shown in Table 2.

Table 2. Foreign ions effect on the Cd(II)-NNPh complex $\mu\text{g mL}^{-1}$.

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
$\text{Na}_2\text{C}_2\text{O}_4$	200
Cd(II)	-
Cr(VI)	8
KCN	30
Mg(II)	600
V(III)	100
Mn(II)	500
Cr(III)	80
Cd(II)	2

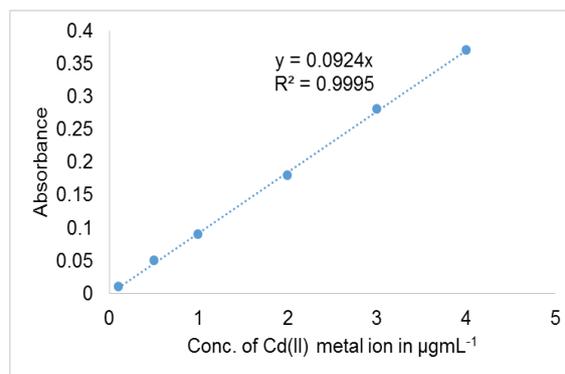


Fig. 7. Calibration graph of Cd (II)-NNPh complex.

IR of Cd(II)-NNPh complex

IR of NNPh have shown stretching band of ν (O-N) ν (O-O) at 3000 cm^{-1} . The band of ν (C=N) ν (N-O), and δ (C-OH) were measured at 1720, 1550, 1220, 1100 and 900 cm^{-1} wave number. Absorption bands in bending region at 1095, 900 and 800 cm^{-1} of nitroso and naphthyl is shown in Fig. 8. The band of metal-chelate shown changed from NNPh reagent. The ν (N-O) stretching band shown increase of 20-30 cm^{-1} due to bonding with N of nitroso group. The ν (C-O-H...N-O) stretching band increased to high band by 20-30 cm^{-1} next to 1750 and 1250 cm^{-1} ν (O-N) bond between Cd NNPh through ν (M-O). The change in absorption bands showed bonding between Cd NNPh chelation through the M-O-H and M-N sites (Korai, MA, 2019). Newest peaks showed at 1440 cm^{-1} the ν (M-O) for Cd(II)-NNPh complex are shown in Fig. 9.



Fig. 8. IR spectra of NNPh reagent.

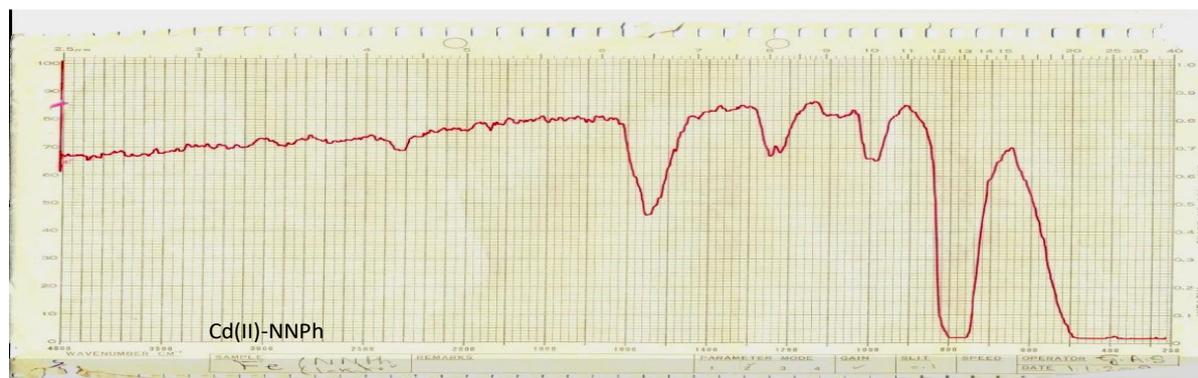


Fig. 9. IR spectra of Cd-NNPh complex.

Validation of method

Proposed method' results were validated with AAS, reference materials, % age recovery test at 95%

confidence interval. Alloy stainless steel 651-7 and Tap water were tested for reliability and accuracy of method; the results are given in Table 3-6.

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

Sample	Metal ion	proposed method (µg mL ⁻¹)	%RSD	AAS method µg mL ⁻¹	RSD%	Recovery
Stain less steel 651-7	Cd(II)	9.29	0.6	9.3	0.5	100.75
GBW01619-Unalloyed steel	Cd(II)	7	6.99	1.3	0.4	99.99

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)	3.7	3.68	2.5	0.5	99.98

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

Analyte ions	Added content (µg mL ⁻¹)	Found (µg mL ⁻¹)	R (%)
Cd(II)	2.25	2.23	99

Table 6. Determination of cadmium in reference materials.

Sample	Certified value of Cadmium (µg g ⁻¹)	Found Cadmium (µg g ⁻¹)	RSD
GBW01620-Unalloyed steel	4.6	4.4	1
HZL205-High tensile steel	0.26	0.25	1.5

GBW01622-Unalloyed steel 1.9 1.8 1.3

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

Sources of the Samples	Samples	Cadmium ($\mu\text{g L}^{-1}$)			
		AAS		Proposed method	
		Found	RSD (%)	Found	RSD (%)
Human Hair(Male)	Hair	59.7	1.3	59.2	1.5
	Blood	2.98	1.6	2.96	1.4
Non-Smoker (Male)	Urine	0.69	1.8	0.66	1.9
	Blood	55.6	2.1	52.8	2.4
Smoker (Male)	Urine	13.8	2.3	13.7	2.5
	Blood	219.7	1.5	219.5	1.3
Kidney disease patient (Male)	Urine	57.5	1.6	57.3	1.6
	Blood	99.6	2.1	99.4	2.3
Hypertension patient (Female)	Urine	29.3	2.2	29.2	2.5
	Blood	59.9	1.6	59.4	1.9
Diabetes patient (Female)	Urine	20.1	1.6	19.7	1.8

Table 8. Determination of cadmium in some fertilizer and Tobacco/Cigarette.

Sample	Cadmium (mg kg^{-1})	
	Found	RSD (%)
Muriate of potash	1.91	1.4
Triple super phosphate	2.61	1.6
Tobacco & Cigarette		
Brand Names or Samples	Cadmium /Cigarette	
	Found	RSD (%)
Entire tobacco	$2.93 \mu\text{g g}^{-1}$	1.7
Capstain	163 ng/Cigarette	1.9
Gold Leaf	198 ng/Cigarette	1.4
Gold Flake	149 ng/Cigarette	1.3

Table 9. Comparison of cadmium investigation using NNPh.

Metals	Procedures	References
Cd(II)	in Tween 80, D.L. $0.039 \mu\text{g mL}^{-1}$	Yun, J. <i>et al.</i> , 2000
Cd(II)	in Triton X-100, $\epsilon 2.05 \times 10^4 \text{ mol}^{-1}\text{cm}^{-1}$, $\lambda_{\text{max}} 425\text{nm}$ $0.02 \mu\text{g mL}^{-1}$	H. Abdollahi <i>et al.</i>
Cd(II)	in 1.0% SDS, $\epsilon 1.02 \times 10^4 \text{ mol}^{-1}\text{cm}^{-1}$, $\lambda_{\text{max}} 579.9 \text{ nm}$, D.L. 5.8 ng/mL	Proposed 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 replaced the old solvent extraction methods which are time consuming, costly and toxic. The results showed good improvement in sensitivity, molar absorption than reported methods as shown in table 9. The proposed method has been applied successfully to the determination of cadmium from biological, environmental, real and industrial samples.

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