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Sepration and determination trace amount of cadmium ions in real and water samples by cloud point extraction - flame atomic absorption spectrophotometry after preconcentration with non-ionic surfactant Triton-X114

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ABSTRACT

2-(3- indolyl) – 4,5 di phynyl imidazole.(IDPI) was used as a complexing agent in cloud point extraction for the first time and applied for selective pre-concentration of trace amounts of cadmium. The method is based on the extraction of cadmium at pH= 7.0 by using non-ionic surfactant Triton-X114 and 2-(3- indolyl) – 4,5 di phynyl imidazole. (IDPI) as a chelating agent. The adopted concentrations for IDPI, Triton X-114 and HNO_3, bath temperature were optimized, The response are linear over concentration range of 8.0-90 (ng mL^{-1}) for Cd^{2+} and RSD % (n =5) 1.8 for Cd^{2+}, Detection limits (3SDb/m, n =10, m = slope of calibration) of 2.8 (ng.mL^{-1}) for Cd^{2+} respectively. The enrichment factors was 33 for Cd^{2+}. the preconcentration factors was 39 for Cd^{2+} respectively. The high efficiency of cloud point extraction to carry out the determination of analytes in complex matrices was demonstrated. The proposed method was successfully applied to the ultra-trace determination of cadmium in real and water samples.

Keywords: 2-(3- indolyl) – 4,5 di phynyl imidazole.(IDPI); cadmium ion; Cloud point extraction; Flame Atomic Absorption Spectrometry

1. INTRODUCTION

The main uses of cadmium include nickel-cadmium batteries, invented by Thomas A. Edson in the early part of the 20th century, and in cadmium coatings for the anti-corrosion protection of steel [1]. Our environment contains countless sources of cadmium and in the modern world this element is ubiquitous in food, water and air. The greatest human cadmium exposure comes from tobacco smoke and food consumption, most of which arises from the uptake of cadmium by plants from fertilizers, sewage sludge, manure and atmospheric deposition [2]. Cadmium is not only regarded as essential to human life, but is now known to be extremely toxic [3,4]. and accumulates in humans mainly in the kidneys[5]. Prolonged intake, even of tiny amounts, leads to severe dysfunction of the kidneys. Cadmium is widely found in society, either in useful products or in controlled wastes. Flame atomic absorption spectrometry due to low cost, speed and ease-of-use is more considered [6]. However, the detection limit for measurement of low levels of cadmium in samples is not suitable, therefore the preconcentration before

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*Corresponding author: gh.vatankhah@gmail.com measurement with flame atomic absorption spectrometry is necessary. The old methods of separating for example a liquid-liquid extraction are used toxic organic solvents which are dangerous to the environment and humans. [7-9] In cloud point extraction method, a nonionic surfactant such as triton X-114 used which due to the non-volatile and non-flammable properties has no great risk to the environment. In addition, in this method small amount of surfactant about 10 mg for each sample is used. Various methods have been used for preconcentration of cadmium, including solid phase extraction [10] and in situ solvent formation micro-extraction (ISFME). [11] Cost of materials used in mentioned methods, especially in situ solvent formation micro-extraction is very high. In cloud point extraction method, analysis cost is very low and requires short time. [12-15]. Cloud point extraction (CPE), employed in analytical chemistry to separate and preconcentrate organic compounds and metal ions, has been well reviewed [16] Cloud point extraction is the process in which the surfactant is added to the aqueous solution which containing the component or components that must be extracted[17]. Surfactants are usually organic compounds that are amphiphilic, meaning they contain both hydrophobic groups (their tails) and hydrophilic groups (their heads). Therefore, a surfactant contains either a water insoluble (or oil soluble) component and a water soluble component. The tail of most surfactants is consisting of a hydrocarbon chain which can be linear, branch or aromatic. [18,19]. Suitable amount of surfactant shall be added to provide the micelles in the solution. It means that the final concentration of the surfactant shall be exceeding from its CMC (Critical Micelle Concentration). Then for micelle or cloud solution formation, conditions (such as increase or decrease in temperature, increase in salt or other surfactants) are changed and with applying the suitable conditions, surfactant molecules form micelles. In order to speed up the separation of two phases, centrifugation can be used. Finally phase separation is done and a surfactant-rich phase and an aqueous phase will observe. [20,21], In this work, a cloud-point preconcentration procedure was introduced for determination of Cd^{2+} ion, after the formation of complex with 2-(3- indolyl) – 4,5 di phynyl imidazole (IDPI). The lipophilic IDPI-Cd^{2+} complexe, completely extracted from aqueous solution to the concentrated micellar medium, and the analytes was ultimately analyzed by flame atomic absorption spectrometry.

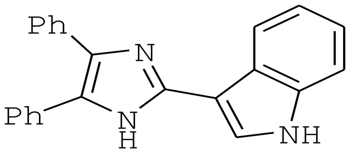
2. EXPERIMENTAL

2.1. Reagents

All solutions were prepared with deionized water. Analytical-grade methanol, acids, and other chemicals used in this study were obtained from Merck. A 1.0% (w/v) Triton X-114 from Merck (Darmstadt, Germany) was prepared by dissolving 1.0 g of Triton X-114 in a 100 mL volumetric flask with stirring. All chemicals such as nitrate of Cd(II) and other cations were of analytical grade purchased from Merck. The 2-(3- indolyl) – 4,5 di phynyl imidazole.(IDPI) was synthesized, purified and characterized according to the literature[22].

2.2. General Procedure for the Synthesis of the Ligand 2-(3- indolyl) – 4,5 di phynyl imidazole.(IDPI)

A mixture of benzil (1mmol), ammonium acetate (3mmol) and substituted benzaldehydes (1mmol), was added silica-bonded N-propylsulfamic acid (0.1 g) in solvent free condition at 80 ^{0}C for the appropriate time. and heated at 80^{0C} in an oil bath. After completion of the reaction, as indicated by TLC, the reaction mixture was filtered and remaining washed with warm ethanol (2-5 mL). After cooling, the corresponding 2,3-dihydroquinazolinone products were obtained which purified by recrystallization from hot ethanol. The recovered catalyst was dried and reused for subsequent runs. The product was purified by column chromatography on silica gel [eluent: EtOAc/n-hexane (1:3)] to give pure2-(3- indolyl) – 4,5 di phynyl imidazole.(IDPI) in 90% yield. (Scheme 1) was synthesized according to literature [22].



Scheme 1. 2-(3- indolyl) – 4,5 di phynyl imidazole.(IDPI)

Mp: 302-305 ºC

^{1}H-NMR (DMSO-d_6,400 Hz) δ: 7.05-7.16 (m, 3H), 7.23-7.28 (m, 3H), 7.37 (d, 3H, J=7.8 Hz), 7.44 (d, 2H, J=7.3 Hz), 7.56 (d, 2H, J=7.1 Hz), 7.93 (d, 1H, J=2.5 Hz), 8.40 (d, 1H, J=8.6 Hz), 11.29 (s, 1h), 12.20 (brs, 1H).

^{13}C-NMR (DMSO-d_6, 100 MHz) δ: 106.8, 111.6, 119.7, 121.5, 121.8, 123.7, 125.1, 126.8, 128.1, 128.7, 136.2, 143.7, 145.3, 171.7.

IR(KBr) (cm^{-1}): 3412, 3055, 1621, 1598, 1491, 1451, 1336, 1208, 1182, 1049, 940, 854, 761, 749, 696.

Elemental analysis: C, 82.36; H, 5.11; N, 12.53.

Found: C, 82.17; H, 5.17; N, 12.29.

2.3. Procedure Cloud -point extraction

For CPE, an aliquot of 15 ml of a solution containing cadmium ion, 0.1 % Triton X-114 and 0.26 mM of IDPI was adjusted to pH 7.0 with HCl. The mixture was kept for 20 min in the thermostatic bath maintained at 50° C. The phase separation is accelerated by centrifuging at 4000 rpm for 15 min. The whole system was cooled in an ice-bath so for 15 min that the surfactant rich phase would regain its viscosity. In this way, the bulk aqueous phase was easily decanted. The remaining micellar phase was dissolved in 500 µl of 2.0 M HNO_3 in methanol and then the cadmium ion content was readily evaluated by FAAS.

2.4. Application to Real Samples

2.4.1. Water samples

Tap, well, natural mineral and sea water samples were collected in acid-leached polyethylene bottles. Bushehr tap water sample was collected from our Lab (Bushehr, Iran). The natural mineral water, well water samples and sea water sample was prepared from Persian Gulf (Iran). were selected from Bushehr and Persian Gulf, respectively in Iran. Al water samples were collected (if needed), filtered through 0.45 µm Millipore cellulose acetate membrane filters to remove particles and diluted with distilled water to the ratio of 1:1. The samples were then adjusted to pH=7.0 and immediately analyzed [23].

2.4.2. Soil samples

Accurately weighed 1.0 g of soil samples from near Bushehr petrochemical center (less than 200 meshes), dried at 110 °C were poured into a 250-mL beaker and 10 ml concentrated nitric acid was added to it. The mixture was gently heated under a hood until drying. After complete dry and the mixture was cooled to room temperature, A second 10-mL portion of concentrated nitric acid was added and the procedure. Then 10 mL concentrated hydrochloric acid was added to the beaker and the mixture was gently heated until complete drying. After cooling, the residue was dissolved in 10 mL of 1 M HCl and the solution was then filtered into a 100-mL calibrated flask, using a syringe filter (0.45 μ m pore sized). The sample was neutralized by proper amounts of a 1 M NaOH solution and finally diluted to the mark with water [24].

2.4.3. Blood samples

Homogenized blood sample 20 mL was weighed accurately and in a 200 mL beaker was digested in the presence of an oxidizing agent with addition of 10 mL concentrated HNO_3 and 2 mL 70 % $HClO_4$ was added and heated for 1 hour. The content of beaker was filtered through a Whatman No. 40 filter paper into a 250 mL calibrated flask and its pH was adjusted to 7.0 and diluted to mark with deionized water [25, 26].

3. RESULTS AND DISCUSSION

The aim of this work was to develop a simple, sensitive and available method for the preconcentration and determination of trace amounts of Cd^{2+} ion in various real samples using flame atomic absorption spectrometry coupled with CPE. In this regard, the influence of various effective parameters including, pH, surfactant and IDPI concentrations, heating time and temperature, centrifuge time and rate, as well as the effect of electrolyte on absorbance, were optimized. The complexation study yields important information about the interaction between the ligand and metal ions. Recently, we have used the spectrophotometric method for this purpose [27], before using IDPI for the CPE of the metal ions.

3.1. Absorption spectra

Atypical Cloud point experiment required the following steps: 25mL solution contain analyte ions, 0.1 % Triton X-114 for Cd^{2+} ion and 0.26 mM Ligand 2-(3- indolyl) – 4,5 diphynyl imidazole (IDPI) was adjusted to related pH =7.0, was adjusted to related Ph= 7.0, the mixture shaken for 15 min and left to stand in a thermostated bath at $50^{C^{\circ}}$for 20 min to Cd^{2+} ion, high viscosity Cloud point formed ,the bulk aqueous phase was easily decanted .The remaining micellar phase was dissolved in ethanol and then the ion content was readily evaluated by UV-Vis spectrophotometry at λ_{max} = 350nm for Ligand 2-(3- indolyl) – 4,5 di phynyl imidazole (IDPI) and λ_{max} = 425nm for complex IDPI - Cd^{2+} ion, as well as calculated distribution ratio values by spectrophotometric method[28]. With dependance on Calibration Curve Fig (1).

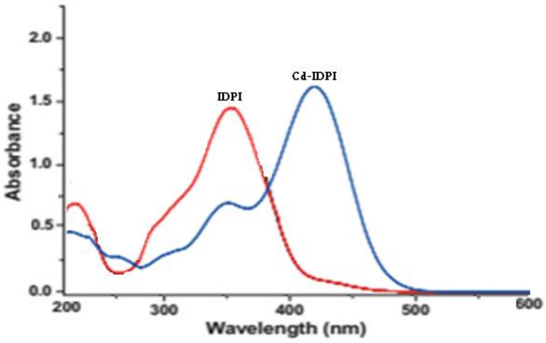


Fig. 1. Absorption spectra of IDPI - Cd complex. Conditions: 0.1% (w/v) Triton X-114, 0.26mM IDPI and 0.05 μg mL^{-1} cadmium ion.

3.2. Effect of pH

A complex with sufficient hydrophobicity is required for separation of metal ions. The mentioned complex can be extracted in a small volume of surfactant-rich phase. The extraction efficiency is dependent on the pH at which complex formation occurs. Therefore, pH is the most important parameter affecting the extraction efficiency and it is necessary to choose the optimum pH at first [29-31]. The effects of pH on to extract metal complexes are given in Fig2. In the pH range of 6.5-7.0, extraction was quantitative. The decrease in recoveries at pH >7.0 is probably due to the precipitation of metal ions in the form of hydroxide, and at pH < 6.5 may be due to competition from hydronium ion toward ions for complexation with IDPI or decomposition of complex at pH <7.0, which led to the decrease in recoveries. In later experiments a pH of 7.0 was selected.

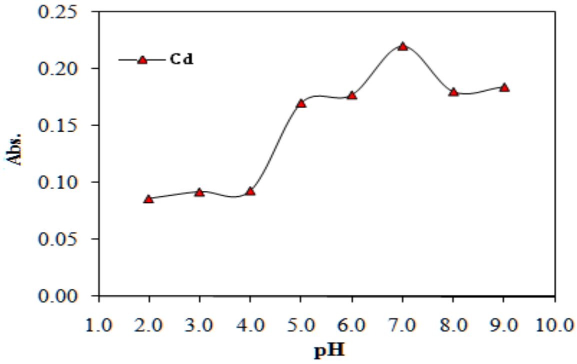


Fig 2. Effect of pH on the extraction recovery of cadmium ion. Conditions: 0.01 mg mL^{-1}, 0.26 mM IDPI, 0.1% (w/v) Triton X-114. Other experimental conditions are described in Procedures

3.3. Effect of IDPI concentration

The absorbance of extracted metal ions as a function of the concentration of IDPI is shown in Figure 3. As can be seen, increasing IDPI concentration up to a 0.26 mM causes increasing absorbance. Thus, a IDPI concentration of 0.26 mM was chosen to optimize other variables. At lower than 0.26 mM of IDPI, insufficient concentration leads to incomplete complexation. A possible explanation for the decrease in absorption with higher concentrations may be attributed to the formation of charged complexes with excess IDPI in the medium or with remaining excess IDPI in aqueous solution, competing with surfactant-rich phase for formation of complex with metal ions in aqueous phase.

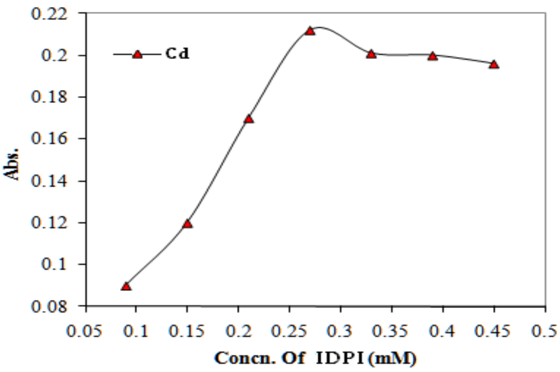


Fig. 3. Effect of IDPI concentration on the extraction recovery of cadmium ion. 0.01 mg mL^{-1}, 0.1% Triton X-114, pH 7.0. Other experimental conditions are described in Procedures.

3.4. Effect of Triton X-114 concentration

Triton X-114 was used as extractant and the concentration of this surfactant affects both the extraction efficiency and the volume of the surfactant-rich phase. In order to obtain easy phase separation and maximum extraction efficiency the optimum amount of Triton X-114 should be determined[32]. The variation in absorbance of extracted Cd^{2+} ion within the Triton X-114 concentration range of 0.015 - 0.15% (w/v) was examined and results shown in Figure 3. The results show that quantitative extraction was obtained with an optimum Triton X-114 concentration of 0.1% (w/v), at which the highest absorbance for extracted Cd^{2+} ion was obtained. For concentrations lower than 0.1% (w/v), the preconcentration efficiency of the formed complexes was very low, since the assemblies at low concentration were probably inadequate to preconcentrate trace amounts of Cd^{2+} ion[33]. The decreasing of absorbance at a concentration higher than 0.1% (w/v) is due to the remaining of some part of Triton X-114 and IDPI in aqueous solution as this phase can compete with surfactant-rich phase to draw analyte ions.

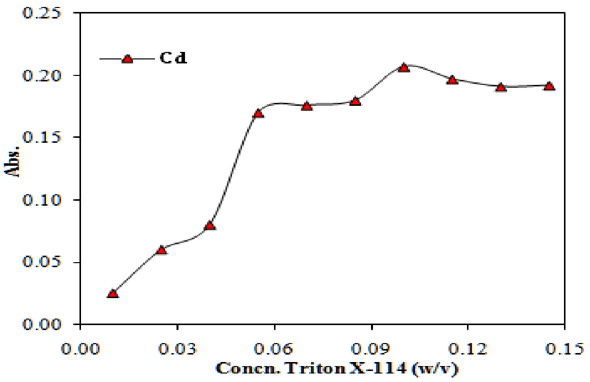


Fig 4. Effect of Triton X-114 on cadmium ion Recovery, Condition: 15 mL 1.0 μg mL^{-1} cadmium ion at various Triton X-114, 0.26 mM IDPI, pH=7.0, 0.2 % (w/v)KCl, eluting solution 0.5ml of 2.0 M HNO3 in methanol.

3.5. Effect of temperature and equilibrium time on CPE

It was desirable to employ the shortest equilibration time and the lowest possible equilibration temperature as a compromise between completion of extraction and separation of phases. The dependence of extraction efficiency upon equilibration temperature and time above the cloud point in the range 30-70 °C and 5-30 min were thoroughly optimized, respectively[34]. Holding the sample solutions for 25 min at 50 °C was found to be satisfactory to achieve a small volume of the surfactant-rich phase, quantitative extraction and experimental convenience.

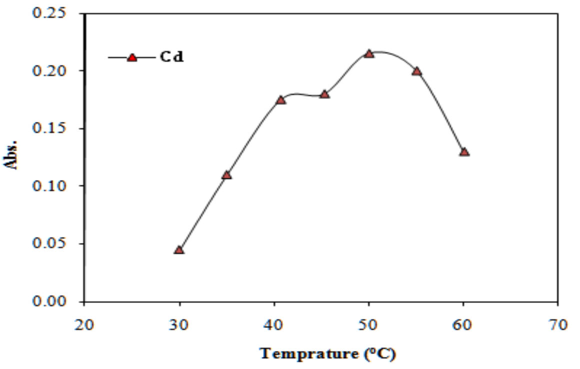


Fig 5. Effect of temperature on cadmium ion recovery, Condition: 15 mL 1.0 μg mL^{-1} cadmium ion at various temperature, 0.1% (w/v) Triton X-114, 0.26 mM IDPI, pH=7.0, 0.2 % (w/v) KCl, eluting solution 0.5ml of 2.0 M HNO_3 in methanol.

3.6. Effects of added electrolyte

The cloud point of micellar solutions can be controlled by addition of salts, alcohols, non-ionic surfactants and some organic compounds (salting-out effects) [35]. To date, most of the studies conducted have shown that ionic strength has no appreciable effect on the extraction efficiency. An increase in the ionic strength in the CPE does not seriously alter the efficiency of extraction of the chemical forms. Moreover, the addition of a salt can markedly facilitate the phase-separation process, as demonstrated with some non-ionic surfactant systems, since it alters the density of the bulk aqueous phase [36,37]. In this way, 2.0 M KCl concentration was used in all further experiments.

3.7. Effect of Diluents type and volume methanol

Since the surfactant-rich phase obtained after the cloud point pre-concentration contains a high concentration of Triton X-114 and, at the same time, the volume obtained is rather small (500µl), methanol containing 2.0 mol L^{-1} HNO_3 was added to the surfactant-rich phase after phase separation. Moreover, it was necessary to decrease the viscosity of the rich phase without excessive dilution of the micelle to facilitate the introduction of the sample into the atomizer of the spectrometer. There is an optimum volume (500µl) with respect to the cadmium ion recovery. Smaller volumes of methanol were not tested because in this case it was not possible to quantitatively transfer the rich phase from test tubes to the graduated tubes and measuring the absorbance. Larger volumes of acidified methanol dilution are clearly predominated resulting in a gradual absorbance reduction. A 500µl volume of methanol was therefore used throughout the remaining experiments.

3.8. Analytical Figure, precision and detection limits of Merit

The calibration graph was obtained by pre-concentration of 15 mL aliquots of standard solutions containing known amounts of the analyte in the presence of IDPI and Triton X-114 at pH=7.0 for CPE of Cd^{2+} ion under the experimental conditions specified in the procedure. Linear relation ships between the absorbance measured and the concentration of the metal ions in the solution was obtained. Table1 shows the parameters of the calibration graphs.

The calibration graph was linear in the range of 8–90 (ng mL^{-1}) for Cd^{2+} ion under the optimum conditions of the general procedure. Some factors that characterize pre-concentration systems, such as the enrichment factor (EF) and the CI were also determined (30). Enrichment factors were calculated as the ratio of the slope of the calibration graph obtained by pre-concentration and direct aspiration, respectively. The CI is defined as the sample volume (mL) consumed to reach a unit of EF: CI =Vs (mL)/EF, where Vs is the sample volume. The precision of the procedure was determined as the RSD of 5 in dependent measurements carried out in solutions containing the ions at 50.0 (ng mL^{-1}). The limit of detection (LOD) defined as the metal concentration giving a response equivalent to 3 times the standard deviation (s) of the blank (n= 10), was also determined. Characteristic data obtained under optimum conditions by pre-concentrating 15 mL of the solution of the ions are given in Table 1. The pre-concentration factor for all ions, calculated by dividing the aqueous phase volume by the final volume of the pre-concentrated phase, is 30, where as the EF values, calculated as the ratio of the slope of the calibration curve of the analytes after pre-concentration to the slope of the calibration curve of the analytes before pre-concentration, are 39 for Cd^{2+} ion, respectively.

Table 1. Parameter of the calibration graphs obtained by the proposed method at optimum conditions for Cd^{2+} ion

Parameters	Ion
	Cd
Linear Range (ng mL^{-1})	8.0 – 900
CI[a]	0/031
Detection Limit (ng.mL^{-1}) (n =10)	2/8
Enrichment factor	33
RSD[b] % (n =5)	1/8
Recovery %	99

[a] CI = consumptive index.

[b] RSD = Relative standard deviation.

Table 2, gives the characteristic performance of the proposed method of standard solutions subjected to the entire procedure. Limits of detection and quantification according to IUPAC are also included. The limit of detection and the linear range of the proposed method are comparable to other methods that also employed FAAS.

Table 2. Optimum Conditions for the Presented CPE Method

Parameter	Optimum Value for ions
pH	7.0
IDPI concentration (mM)	0.26 mM
Triton X-114 (w/v)	0.1 % (w/v)
Eluting agent	0.5 mL 2.0 mol L^{-1} HNO$_3$ in methanol
Bath temperature	50^{0C}
Temperature time	20 min
Centrifuge time	15 min
Centrifuge rates	4000 rpm

3.9. Interfrences Selectivity

In view of the high selectivity provided by flame atomic absorption spectrometry, the only interferences studied were those related to the preconcentration step. Cations that may react with IDPI, and anions that may form complexes with the metal ions were studied [38-40]. The determination of Cd^{2+} ions in the presence of some metal ions, including Na^+, K^+, Ni^{2+}, Cu^{2+}, Pb^{2+}, Co^{2+}, Sn^{2+}, Ag^+, Fe^{2+}, Zn^{2+} and Fe^{3+} The species were considered as interference if they caused an analytical variation of 5% or more when compared to the analytical signal obtained in the absence of the interfering species. At the applied pH value, no interference was observed from even 50-fold excess of the interfering ions.

3.10. Determination of Cd^{2+} ion in real samples

To validate the proposed method, the developed procedure was applied to the determination metal ions in real samples. For this purpose, 15 mL of each of the samples were pre-concentrated with 0.1% (w/v) Triton X-114 and IDPI concentration of 0.26mM, following the proposed procedure. The results are shown in Table 3 and 4.

Table 3. Determination of Cd^{2+} ion in blood and soil

Ion		Blood			Soil		
	Added (μg.mL^{-1})	Found (μg mL^{-1})	RSD%	Recovery%	Found (μg mL^{-1})	RSD %	Recovery %
Cd	0 15	2.3 17.1	1.4 1.6	- 98.0	4.5 20.0	1.3 1.5	- 103.0

Table 4. Determination of Cd^{2+} ion in Waste water (Hospital), River water and Tap water

Sample	Added (μg mL^{-1})	Founded (μg mL^{-1})	RSD %	Recovery %
Waste water(Hospital)	0 15	10.33 16.19	1.1 1.8	--- 103.1
River water	0 15	6.18 16.43	1.1 1.3	--- 95.3
Tap water	0 15	2.21 16.69	2.1 1.8	--- 102.4

4. CONCLUSIONS

The micellar extraction of Cd^{2+} ion with IDPI in to the phase of non-ionic surfactant TritonX-114 has been investigated. The proposed cloud point extraction method, using ligand 2-(3- indolyl) - 4,5 di phynyl imidazole.(IDPI), as a stable and fairly selective complexing agent offers a simple, rapid, inexpensive and environmentally benign methodology for preconcentration and separation of Cd^{2+} ion in aqueous solutions. This method gives very low LOD, good RSD and was applied to the determination of trace amounts of Cd^{2+} ion in various real samples. In a full comparison of presented results in this paper with those previously reported, it is found that this method is superior in terms of linear range, detection limits and selectivity. For comparison, the analytical performance data of similar method reported in literature have been listed in Table 4 and 5. In a view glance to the results one can notice that present method is superior to those previously reported in term of some characteristics performances [41-43].

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