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Cloud Point Extraction and Flame Atomic Absorption Spectrometric Determination of Lead and Cadmium in Natural Waters

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A pre-concentration method for low concentrations of lead and cadmium in natural water using cloud point extraction is proposed. The analytes were complexed with O,O-diethyldithiophosphate and then Triton X-114 was added as a surfactant. The parameters affecting the pre-concentration efficiency were optimized. The proposed method was applied satisfactory for the determination of lead and cadmium concentrations in natural waters.

Key Words: Cloud Point Extraction, Natural waters, Flame Atomic Absorption, Lead, Cadmium.

INTRODUCTION

Cadmium and lead are of public interest because of several dangerous effects that they may be cause to humans. They are widely dispersed in the environment and exposure to either elements can increase the adverse health effects due to their toxicity after accumulation in multiple organs in human body[1,2]. Cadmium is known as a toxic and carcinogenic element. It is one of the most hazardous environmental pollutants. Lead is also a trace heavy metal of great importance in environmental protection. It is well-known as a toxic element that can affect many organs and causes mental retardation especially in children[3,4]. Therefore, the measurement of trace levels of cadmium and lead in environmental samples is becoming increasingly important. During the last decade, the development of a fast and efficient method for their determination have been the subject of various studies[5,6].

In recent years concern has increased over the concentration of cadmium and lead in waters and the threshold limits of these two elements is continuously decreased by Environmental Protection Agency (EPA) and European Community (EC), which requires greater sensitivity in measurement than it is offered by flame atomic absorption spectrometry (FAAS).

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Several analytical techniques such as graphite furnace atomic absorption spectrometry (GF-AAS)[7], inductively coupled plasma atomic emission spectrometry (ICP-AES)[8] and inductively coupled plasma mass spectrometry (ICP-MS)[9] are available for the determination of trace metals with sufficient sensitivity for most of applications. However, the determination of trace metal ions in natural waters is difficult due to various factors particularly their low concentration and matrix effects. Pre-concentration and separation can solve these problems and lead to a higher confidence and easy determination of trace elements by less sensitive but more accessible instruments such as FAAS. So far, the conventional methods used for the pre-concentration of metal elements include; liquid-liquid extraction, evaporation and solid phase micro-extraction[10,11] have been reported. Among the different pre-concentration methods, cloud point extraction is superior for pre-concentration of trace metals in respect to minimum solvent waste generation and efficient transferring of the target elements into the surfactant-rich phase. As a result, much interest has recently been shown in using cloud point extraction for pre-concentration of elements[12,13]. Aqueous solution of non-ionic surfactants may separate in a narrow temperature range called the cloud point. Watanabe *et al.*[13,14] first studied and reported this extraction method using different complexing agents for the pre-concentration of some elements.

The present paper describes the application of cloud point extraction using O,O-diethyldithiophosphate (DDTP) as a complexing agent and Triton X-114 as non-ionic surfactant to the separation and pre-concentration of Cd and Pb in surface waters.

EXPERIMENTAL

The non-ionic surfactant Triton X-114 (Fluka Chemical Co.) was used in extraction. Standard solutions of cadmium and lead (BDH Ltd) were diluted from the commercial stock standard solutions of 1000 µg mL^{-1} for atomic absorption spectrometry using 0.1 N nitric acid. 10 % (m/v) of the ammonium salt of DDTP was prepared freshly and purified in a column containing C18 immobolized on silica gel.

Distilleddeionized water was used for preparation or dilution of stan7dard samples. All glassware was placed into 25% (v/v) nitric acid for 24 h before use. After removal from acid, the vessels were rinsed with distilled de-ionized water and dried.

Determination of cadmium and lead in the extracts were carried out on a Varian atomic absorption spectrometer, Model AA-220. The system was equipped with a deuterium lamp for background correction. The Varian standard hollow cathode lamps of Cd and Pb were used in the determinations. The Instrumental conditions are summarized in Table-1.

TABLE-1
INSTRUMENTAL CONDITIONS FOR THE DETERMINATION OF Pb AND Cd

Element	Wavelength	Type of Flame	Condition of flame	Slit	Lamp current	Expansion factor
Pb	217.0 nm	Air-C_2H_2	Oxidation	1.0 nm	5 mA	1
Cd	228.8 nm	Air-C_2H_2	Oxidation	0.5 nm	4 mA	1

Sample collection: The water samples were collected from the two rivers; Zayandeh-Rud and Bazoft. Zayandeh-Rud is the most important river in the central part of Iran. It flows through the agricultural and industrial areas in Isfahan province. Bazoft is in Chaharmohal province and no industrial area is located around the river. Samples were taken from different sampling sites and transferred to the laboratory in pre-cleaned glass vessels and prepared for analysis.

Procedure: To 40 mL of sample aliquot or standard solution The DDTP solution was added in order that the final concentration of DDTP reaches to a 1 % (w/v). Triton X-114 was then added so that its final concentration reached to 0.05 % (w/v) acidified with HCl volume was made to 50 mL. The mixture was kept in a refrigerator for 12 h. The mixture was then heated at 40ºC for 15 min to separate the phases. The mixture was centrifuged at 30ºC and 5000 rpm for 15 min. The surfactant-riched phase was separated by removing the aqueous phase by a syringe. The surfactant-rich phase in the tube was reacted with 1 mL of a mixture of 60 % (v/v) methanol and 40 % (v/v) water and 1 % nitric acid.

RESULTS AND DISCUSSION

In order to achieve the better pre-concentration efficiency the different parameters affecting the cloud point pre-concentration process include; pH, amount of DDTP and the amount of Triton X-114 were optimized. The extractions were then performed at the optimized conditions.

Effect of pH: The effect of pH on the pre-concentration efficiency was investigated. The results are shown in Fig. 1 and indicated that for both elements the maximum pre-concentration efficiencies were obtained in acidic region (pH = 1).

Effect of Triton X-114 concentration: Triton X-114 always used in cloud point extractions since it has many advantages which include low toxicity, commercially available in high purified homogeneous form and low cost. 40 mL of solution containing all the reagents in the presence of Triton X-114 with concentrations from 0.02 to 0.20 % (m/v) were used for cloud point extraction. The results obtained from this investigation are shown in Fig. 2 and indicate that a concentration of 0.08 (m/v) is most suitable for pre-concentration of the both elements.

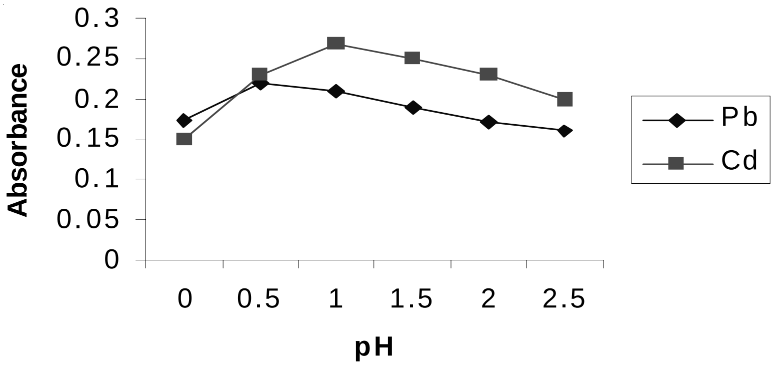

Fig. 1. Influence of pH on the pre-concentration efficiencies of the Pb (200 µg/L) and Cd (100 µg/L) by cloud point extraction

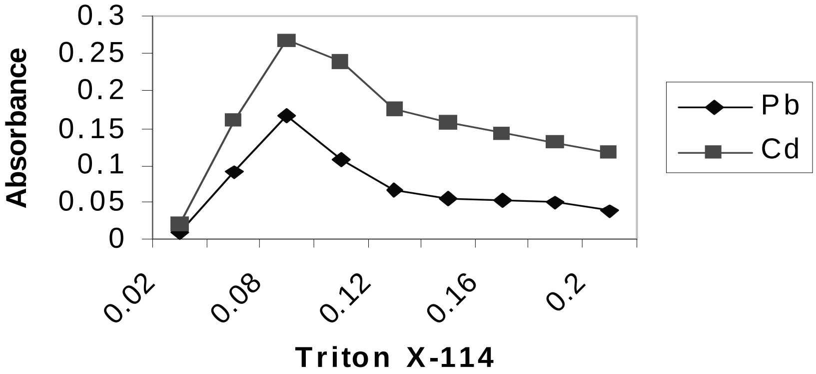

Fig. 2. Effect of Triton X-114 concentration on the pre-concentration efficiencies of Pb and Cd

Effect of DDTP: The effect of DDTP concentration on the pre-concentration efficiencies of Pb and Cd was investigated. On the 40 mL of a solution that contained all the reagents, different amounts of DDTP ranging from 0.05 to 3.20% (m/v) in presence of 0.08 (m/v) of Triton X-114 was added. The results obtained from this investigation are shown in Fig. 3. It can be concluded that increase in the concentration of DDTP causes reduction in pre-concentration efficiency. It could be because of forming charged complex that could not be extracted.

Eeffect of viscosity: After the separation of phases, 1 mL of the methanolic acid was added to the surfactant-rich phase in order to reduce the viscosity. Since the viscosity can affect on the nebulization efficiency and the sensitivity of the system. The effect of methanol concentration in the methanol mixture against the absorbance is shown in Fig. 4.

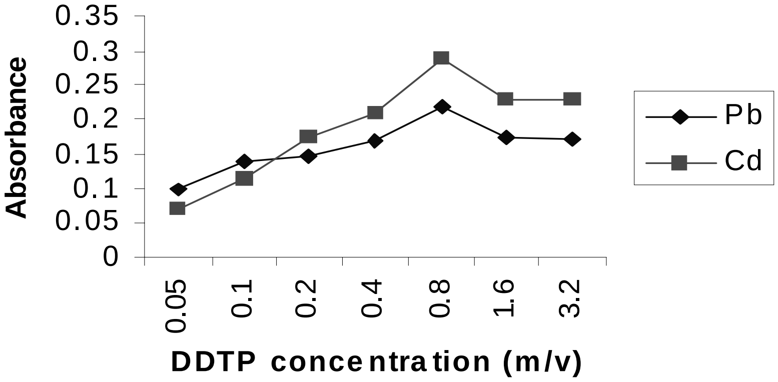

Fig. 3. Effect of DDTP concentration on the pre-concentration Pb (200 µg/L) and Cd (100 µg/L) by cloud point extraction efficiencies of Pb and Cd

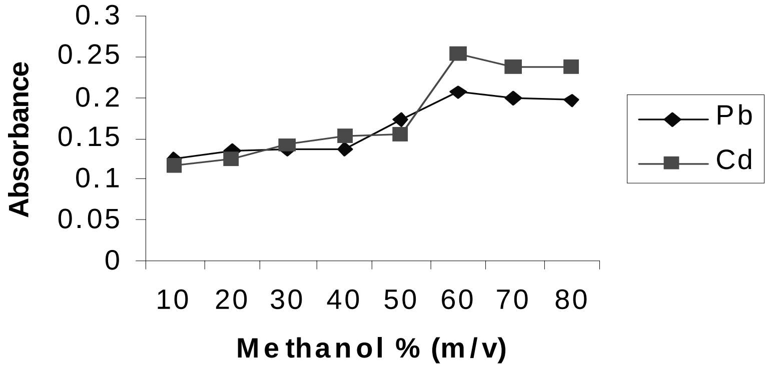

Fig. 4. Effect of methanol percentage on the pre-concentration efficiencies of Pb and Cd

Figures of merit: Calibration curves were obtained by pre-concentrating of 40 mL of sample containing known amounts of lead and cadmium under the optimized experimental conditions. The calibration curve was linear up to 150 µg/L for cadmium and it was linear up to 300 µg/L for lead. The pre-concentration factor was calculated as the ratio of the slope of the calibration curve with pre-concentration to that without pre-concentration. Table-2 shows the analytical characteristics of the method.

Determination of Pb and Cd in surface waters: The proposed method was applied to the determination of Pb and Cd in natural waters. The water samples were collected from two rivers filtered through a Millipore 0.45 µm pore size membrane and used for analysis. The capability of the method was checked by recovery experiments. Table-3 shows the results and demonstrates that the method is quite reliable to determine the concentrations of Pb and Cd at trace level in natural waters.

TABLE-2
ANALYTICAL CHARACTERISTICS OF THE METHOD

Parameter	Pb	Cd
Concentration range (µg/L)	300	150
LOD (µg/L)	0.006	0.007
RSD (%)	3.9	3.2
Correlation coefficient (r^2)	0.998	0.994
Pre-concentration factor	28	34

TABLE-3
RECOVERY OF Pb AND Cd FROM NATURAL WATERS

Sample	Lead (µg/mL)		Recovery (%)	Cadmium (µg/mL)		Recovery (%)
	Added	Founded		Added	Founded	
Zayandeh-Rud	0.00	0.97 ± 0.04	-	0.00	0.12 ± 0.02	-
river water	1.00	1.95 ± 0.05	98.9	0.50	0.63 ± 0.02	101.6
Bazoft	0.00	0.36 ± 0.02	-	0.00	0.08 ± 0.01	-
river water	1.00	1.34 ± 0.03	98.5	0.50	0.57 ± 0.03	98.3

The concentrations of Pb and Cd throughout the river Zayandeh-Rud were determined and showed that as the river passes through the agricultural and industrial areas the levels of Pb and Cd continuously increase (Fig. 5). It is serious treat for the Gavkhooni wetland ecosystem and its valuable biodiversity that finally receive the river water.

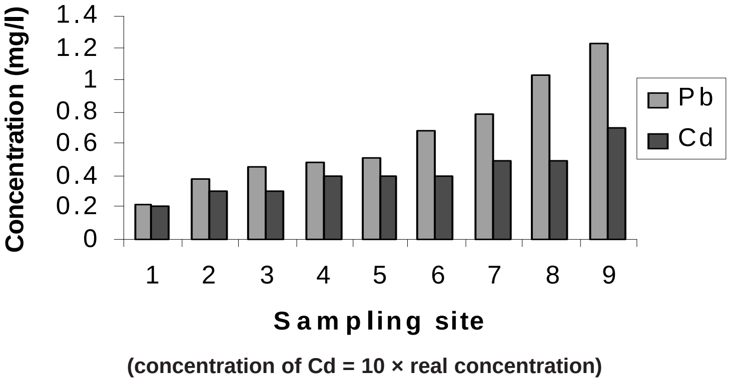

Fig. 5. The concentrations of Pb and Cd throughout the river Zayandeh-Rud

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