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Research Article

Separation and determination of Pb (II) ions from aqueous media by cloud point extraction

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ABSTRACT

A simple, effective and highly selective cloud point extraction procedure was performed for enrichment of Pb (II) from aqueous matrix. The process depends on the formation of a stable complex between Pb (II) ions and Azure A compound at pH 6.0. The formed complex was extracted into micelle phase “Tergitol-NP7” at 25°C. This method was used for preconcentration of Pb (II) before its determination by FAAS. The values of limit of detection and limit of quantification were determined as 2.5 and 4.7 µg l^{-1}, respectively. The enrichment factor of the method was determined as 10 for 50 ml sample volume. Pb^{2+} analyte was quantitatively extracted and successfully determined in the presence of the most common foreign ions. The proposed method was then employed for the analysis of Pb (II) in natural and wastewater samples.

Keywords: Azure A, cloud point extraction, lead determination, TNP7.

Pb (II) iyonlarının bulutlanma noktası ekstraksiyonu ile sulu ortamdan seçici olarak ayrılması ve tayini

ÖZ

Pb (II) iyonlarının sulu ortamdan zenginleştirilmesi için basit, etkili ve oldukça seçici bir bulutlanma noktası ekstraksiyon prosedürü gerçekleştirilmiştir. Proses, pH 6.0' da Pb (II) iyonlarıyla Azür A bileşiği arasında kararlı bir kompleks oluşumuna bağlıdır. Oluşturulan kompleks 25°C'de “TNP7” misel fazı içerisine ektrakte edilmiştir. Bu yöntem, Pb (II)’nin FAAS ile tayin edilmesinden önce önderiştirilmesi amacıyla kullanılmıştır. Tayin sınırı ve gözlenebilme sınırı değerleri sırasıyla 2,5 ve 4,7 µg l^{-1} olarak belirlenmiştir. Yöntemin zenginleştirme faktörü, 50 ml numune hacmi için 10 olarak saptanmıştır. Pb^{+2} analiti, kantitatif olarak ekstrakte edilmiş ve en yaygın yabancı iyonların varlığında başarıyla tayin edilmiştir. Önerilen yöntem daha sonra doğal ve atık su numunelerindeki Pb (II) analizi için kullanılmıştır.

Anahtar Kelimeler: Azür A, bulutlanma noktası ekstraksiyonu, kurşun tayini, TNP7.

1. INTRODUCTION

Water is considered as an essential and valuable resource for all living organisms.[1,2] The rapid development of industrial activities in the past few decades has caused pollution and reduced water quality. Industrial wastewaters can contain heavy metal ions such as lead, arsenic, mercury, nickel, cobalt and chromium.[3] These heavy metals from various industries, such as metal coating industries, mining, tanneries, paint, batteries, fertilizers pollute the waters.[4] Industrial waste containing contaminants can disrupt a huge harm to the aquatic ecosystem by deteriorating the quality of both surface and ground waters and can cause serious damage and bad effects on the existing ecosystem.[5] The atom electron shell structure of these heavy metals identifies their reactivity, complex forming tendencies, physical and biochemical activities.[6]

High concentration of the heavy metals with a certain value may cause serious health problems. The heavy metal toxicity may harm the central nervous activities, damage the liver, lungs, kidneys and some other main organs. Also longer exposure times may cause muscular dystrophy, Alzheimer's disease and several types of

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cancer.[7] Among these heavy metals, lead is a toxic and non-biodegradable metal which is employed in industries such as vehicle manufacture, lubricants, additives, brake pads, tires, insecticides, ceramic products, batteries and dyes.[8]

Exposure to lead may cause the cancer, anaemia, kidney disease, and mental retardation. Lead adversely affects nervous system, gastro-intestinal track, kidneys, reproductive system and also cause encephalopathy, neuro-behavioral deficits.[9] Due to all these adverse effects, the determination of heavy metals in waters is of prime importance for human and environment health.[10] Consequently, many technologies such as adsorption,[11] chemical precipitation,[12] flocculation,[13] ion exchange and membrane filtration.[14] have been used for the determination and removal of Pb(II) ions from wastewater samples.

The cloud point extraction (CPE) technique is one of the most effective techniques for preconcentration of trace metals because of its simplicity, rapidity and environmental compatibility.[15] This technique is based on the phase separation formed in aqueous solutions of non-ionic surfactants which becomes cloudy when heated to a known temperature called as the cloud point temperature (CPT). This causes to the form of two separate phases.The first phase contains the analytes surrounded by surfactants (water insoluble surfactant-rich phase) and the aqueous phase that contains matrix ions. The total volume of the surfactant containing rich phase is much smaller than the aqueous one and that allows very high preconcentration factors for analytes.[16]

In literature, there are studies focused on preconcentration and determination of heavy metal ions based on CPE method. CPE has been used for the preconcentration of lead, after the formation of a brillant cresyl blue dye and the lead has been analysed by flame atomic absorption spectrometry (FAAS) using surfactant TritonX-114,[16] There are also simultaneous preconcentration and determination studies with CPE method. For example, various metals such as copper manganese and nickel have been simultaneously extracted after their complexation with 2-amino-6-(1,3-thiazol-2-diazeyl)-phenol at pH 7[17] and analysed by FAAS, using TritonX-114 as the surfactant.

In this study a highly selective cloud point extraction procedure for separation, preconcentration and determination of Pb (II) ions as its Azure A complex in wastewater samples was developed. Determination of Pb (II) ions were performed by FAAS. The optimum conditions for quantitative recoveries were investigated.

According to our literature survey, the combination of Azure A and Tergitol NP7 for lead preconcentration has not been used before in cloud point extraction.

2. MATERIALS AND METHODS

2.1. Reagents and solutions

The non-ionic surfactant Tergitol NP7 was purchased from Sigma Aldrich. A 1 x 10^{-3} mol l^{-1} of Azure A complexing agent solution was prepared by dissolving appropriate amount of Azure A in distilled water. Pb^{2+} stock standard solution was prepared by dissolving pure $Pb(NO_3)_2$ in distilled water. Pb^{2+} solutions with different concentrations were prepared by diluting from the stock solution. Phosphate and citrate buffer solutions were prepared and used in the experiments. The calibration curves have correlation coefficients of 0.999. A sample of the calibration curve used in the experiments is given in Figure 1.

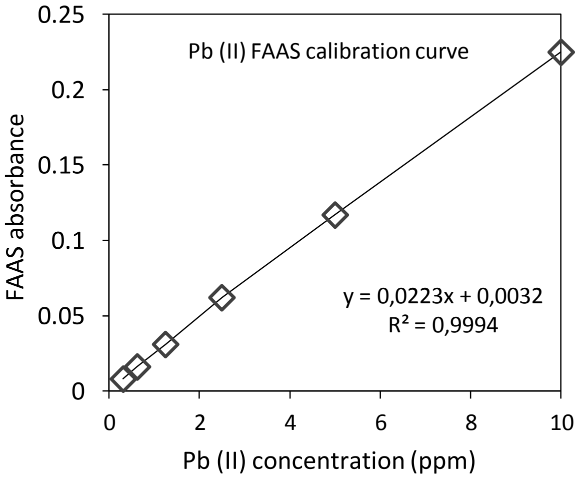

Figure 1. Calibration curve of Pb (II) used in the experiments.

2.2. Apparatus

The absorbance values of Azure A and Pb (II)–Azure A complex were determined by using Shimadzu UV–160A ultraviolet/visible spectrophotometer. The atomic absorbance values of Pb (II) ions were measured by using Shimadzu AA 7000 flame atomic absorption spectrometer and a lead hollow cathode lamp. The atomic absorption signal of Pb was measured as a peak height versus analytical curve. A Nuve BM 402 model thermostatic bath (Nuve Ltd. Turkey) was used to obtain the desired cloud point temperatures. The phase separations were performed by a Nuve NF 400 model centrifuge. The pH measurements of the solutions were conducted by a WTW level 1 model pH meter.

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2.3. CPE test procedure

The cloud point extraction procedure was operated by using the designed model test solutions. A 40 ml of test solution containing 25 mg Pb (II) ions were transferred into a plastic tube. A 0.35 ml of of Azure A solution of 1 x 10^{-3} mol l^{-1}, a 0.5 ml of 2% (v/v) TNP7 surfactant, and a 4.0 ml of buffer solutions of pH 6 were added on it. The centrifuge tube was filled with covered. After shaking the final solution, taken into a thermostatic bath at 30°C for 10 min. Then this solution was centrifuged to separate Pb(II)–Azure A metal chelates from the other matrix at 4000 rpm for 5 min. The aqueous phase was removed and the highly viscous surfactant rich phase was dissolved by adding 1.0 ml, 1 mol l^{-1} HNO_3 in methanol. This final solution was transferred into a 5 ml volumetric flask and the original tube washed with small aliquots of 1 mol l^{-1} HNO_3 in methanol. The final dilution was to 5 ml. The Pb (II) concentration of the final solution was measured by FAAS. All experiments were conducted triplicate.

3. RESULTS AND DISCUSSION

The optimization of the method was examined by changing one variable at a time concept. The main analytical parameters such as solution pH, concentrations of chelating agent and surfactant, incubation time, experiment temperature, sample volume, and matrix ions were optimized.

3.1. The UV-Visible spectrum of Azure A and Pb (II)–Azure chelates

Azure A (3-amino-7-(dimethylamino)phenothiazin-5-ium chloride) is a sulphur and nitrogen contaning water soluble organic dye used in industry and some scientific researches about corrosion inhibitors.[18-20] In this study, it is used as a chelating agent. The chemical structure and UV-Vis spectrum of aqueous Azure A solution and Pb (II)–Azure A complex solution are given in Figure 2.

According to UV-Vis. spectra of Azure A and Pb(II)–Azure A complex, three absorption bands are observed at 240 nm, 290 nm and 630 nm. These bands are identical both for dye and complex. On the other hand, the band at 210 nm was appeared after mixing the Pb(II) and Azure A. This can be considered as an evidence to the formation of the Pb(II)–Azure A complex.

3.2. Effect of Solution pH

In the CPE method, the pH value of the solution constitutes one of the most important steps in the extraction of Pb (II) ions. Because, the metal chelating capability and the stability of the Pb(II)–Azure A complex directly effects the extraction efficiency, and Solution pH is also the main reason for changing them. To gain the optimum extraction efficiency, the solution pH was investigated between pH 2–8 which is adjusted by using phosphate, ammonium and acetate buffer solutions. The results are given in Figure 3.

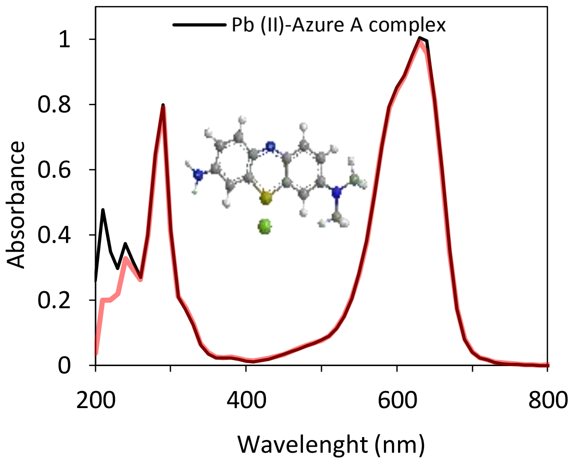

Figure 2. The 3D chemical structure and UV/Vis. spectrum of aqueous Azure A and Pb (II)–Azure A complex.

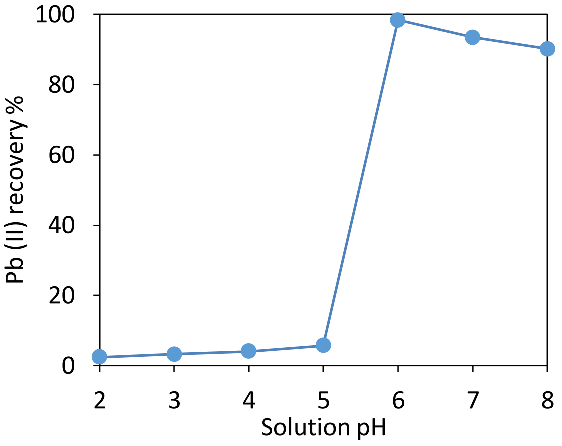

Figure 3. Recovery of Pb(II) ions at different solution pHs.

The optimum recovery value was obtained at pH 6 as given in Figure 3. Consequently, pH 6 value was selected as the most appropriate solution acidity and therefore rest of the experiments were performed at pH 6.

3.3. Concentration of Azure A ligand

Figure 2 clearly indicates that Pb (II) ions and Azure A molecules form a complex. Therefore, the effect of Azure A concentration on the CPE recovery of Pb (II) ions was investigated using volumes from 0.05 to 0.6 ml for solution of 1 x 10^{-3} mol l^{-1}.

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The results are shown in Figure 4. From Figure 4, it is clearly seen that the recovery of Pb (II) ions increases up to 98.2% at 0.35 ml of Azure A and remains stable after this value. So, the 0.35 ml of Azure A was selected for preconcentration of Pb(II) ions for further experiments.

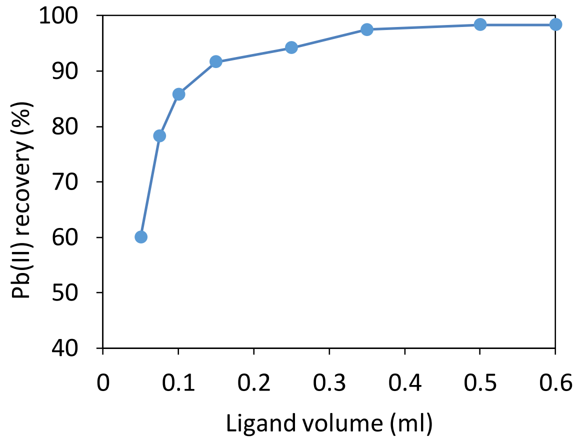

Figure 4. Effect of Azure A volume on the recovery of Pb(II) ions at pH 6.

3.4. Effect of surfactant concentration

In the CPE method, for extraction of Pb(II), choosing an appropriate surfactant and optimization of its concentration is important. Therefore, the effect of TNP-7 surfactant concentration on the CPE recovery of Pb(II) ions was studied using volumes between 0.10 and 3.0 ml from 2% stock solution. The results obtained are given in Figure 5.

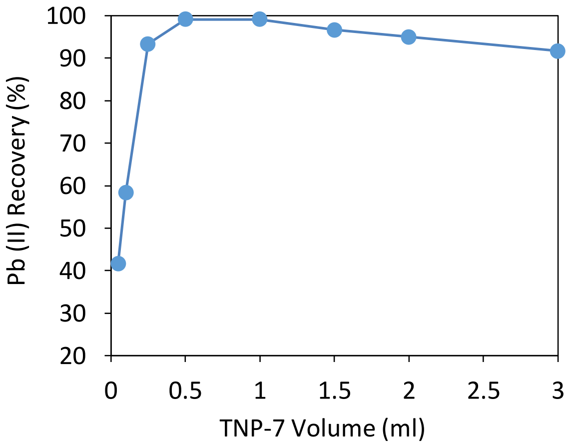

Figure 5. Effect of surfactant concentration on the recovery of Pb(II) ions for 0.35 ml Azure A at pH 6.

As it can be seen from the Figure 5, a 0.5 ml of TNP-7 surfactant is optimum for the quantitative recovery of Pb(II) ions (99.2%). Therefore, a surfactant volume of 0.5 ml was chosen as optimum and the further studies were conducted with 0.5 ml of TNP-7.

3.5. Effect of temperature

Optimizing the temperature of the CPE medium is of prime importance to gain high extraction efficiency and to avoid insufficient phase separation. In CPE analysis, it is necessary to use a low extraction temperature as the temperature affects both the stabilization of metal complexes and the separation of the surfactant-rich phase from the aqueous medium. The surfactant TNP-7 used in this study has a very low cloud point temperature (CPT = 20°C) than other non-ionic surfactants. This allows a very low phase separation temperature and prevents energy consumption. The effect of the temperature was analyzed by varying from 20 to 60°C, and the results showed that the extraction efficiencies were quantitative and stable for temperatures up to 45°C and then decreased (Figure 6). This decrease can be attributed to the lower stability of Pb(II)–Azure A complex at high temperatures. As a result, the 25°C was applied as optimum value for further experiments.

3.6. Effect of interfering ions

The Azure A organic compound was used as chelating agent to bind with Pb(II) ions. However, the possibility of its complexing with several transition metals, alkaline, alkaline-earth and other ions in aqueous media was investigated at pH 6. The tests were made with each ion separately. Obtained results are given in Table 1.

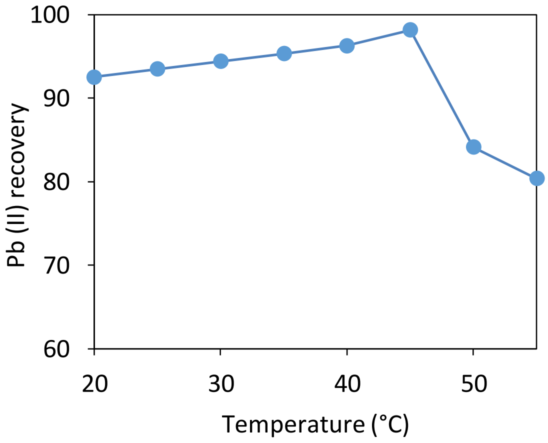

Figure 6. Effect of temperature on the recovery of Pb(II) ions.

The consequences in Table 1 clearly indicate that there is no significant effect of interfering ions on the

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quantitative recovery of Pb(II). Therefore, the CPE method can safely be applied for preconcentration and determination of lead ions in aqueous media and can be detected by FAAS.

The selectivity of the Azure A complexing agent was also studied in the presence of other chelatable transition metal ions such as Cu(II), Cd(II) and Ni(II) to prove the selectivity for all pH values. The results obtained are given in Figure 7.

Table 1. Effect of interfering ions on the recovery of Pb(II) ions for 0.35 ml Azure A at pH 6

Ion	Added as	Concentration (mg l^{-1})	% recovery Pb(II)
Mn^{2+}	$Mn(NO_3)_2.4H_2O$	50	96 ± 3[a]
Cr^{3+}	$Cr(NO_3)_3.3H_2O$	50	95 ± 1
Al^{3+}	$Al(NO3)_3.9H_2O$	50	95 ± 2
Bi^{3+}	$Bi(NO_3)_3.5H_2O$	100	96 ± 3
Na^{+}	$NaNO_3$	1000	98 ± 4
K^{+}	KNO_3	1000	97 ± 4
Ca^{2+}	$CaCl_2$	1000	96 ± 3
Mg^{2+}	$Mg(NO_3)_2.6H_2O$	1000	95 ± 2

[a] Mean ± standard deviation

The tolerable concentrations of the interfering ions were selected as difference in the analytical signal of Pb(II) which is not higher than 5%, when compared with the signal of 5.0 µg l^{-1} Pb(II) in isolated solution. Figure 7 explains there is no possible competitive chelating effect at any pH which may reduce the potential complexing between Azure A and lead ions and decrease the recovery of Pb(II) ions.

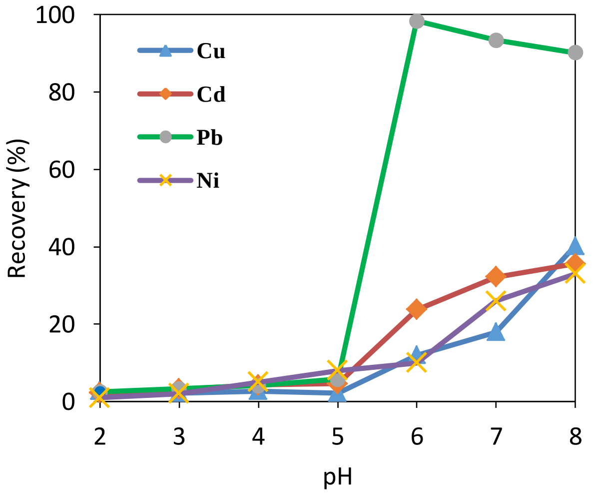

Figure 7. Effect of other metal ions on the recovery of Pb(II) ions for 0.35 ml Azure A and 0.5 ml TNP-7 at pH 6.

3.7. Analytical performance of the CPE method

The analytical characteristics of the cloud point extraction method such as preconcentration factor, limit of detection and quantification were determined. The results obtained are given in Table 2. The limit of quantification (LOQ) and the limit of dedection (LOD) were defined as LOQ = 10 Sd/m and LOD = 3 Sd/m, respectively (where *m* is the slope of calibration curve, Sd is the average standard deviations of 21 blank solutions. The relative standard deviation (RSD) was found by using ten replicate measurements of standard solutions of Pb (II).

Table 2. Analytical characteristics of the method

Parameters	Pb(II)
Limit of detection, µg l^{-1}	2.5
Limit of quantification, µg l^{-1}	4.7
Preconcentration factor	10
Relative standard deviation, %	4
Calibration curve	A = 0.0223C+0.0032
Correlation coefficient, R^2	0.9994

3.8. Real sample analysis

Analyte addition tests for Pb(II) ions were performed on two natural and one industrial waste water samples to validate the optimized method. pH of samples was adjusted to 6 and the CPE procedure was applied to samples and the results are given in Table 3.

Table 3. Analyte addition-recovery test in different water samples by developed CPE method (N = 3)

	Pb		
Samples	**Added (µg)**	**Found (µg)**	**Recovery (%)**
Natural spring water I	-	BDL	-
	5.0	5.09 ± 0.28[a]	102 ± 4
	10.0	9.78 ± 0.23	98 ± 2
Natural spring water II	-	BDL	-
	5.0	5.12 ± 0.19	102 ± 2
	10.0	10.15 ± 0.44	101 ± 3
Factory wastewater	-	BDL	-
	5.0	5.05 ± 0.36	101 ± 4
	10.0	10.22 ± 0.47	102 ± 5

[a] Mean ± standard deviation, BDL: Below detection limit

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4. CONCLUSIONS

An effective and highly selective cloud point extraction method was established for the preconcentration of Pb(II) ions in natural and waste water samples prior to their flame atomic absorption spectrophotometric determination. The results revealed that the Azure A ligand was highly selective for Pb(II) ions between pH 5 and pH 8 region. The pH studies showed that the recovery values of the Pb(II) was quantitative in the presence of Cu(II), Cd(II) and Ni(II) ions under the same circumstances. It was concluded that this phenomenon could be explained by the affinity of the Azure A ligand to Pb (II) ions. It was also obvious that this tendency was because of the chemical compatibility between the Azure A and Pb(II). The proposed method is inexpensive and easy to operate. The analytical performance of the method in the presence of interfering ions was excellent for the detection of Pb (II) ions. As a result, the developed method may be considered as a useful tool for preconcentration and determination of Pb(II) in water samples for routine quality controls.

Conflict of interests

I declares that there is no a conflict of interest with any person, institute, company, etc.

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