ON-LINE PRECONCENTRATION IN FLAME ATOMIC ABSORPTION SPECTROMETRY

ALEVLİ ATOMİK ABSORPSİYON SPEKTROSKOPİSİ İLE SÜREKLİ SİSTEMDE ÖNDERİŞTİRME

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Graduate School of Natural and Applied Sciences,

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ABSTRACT

The submitted study was aimed to developing a simple on-line preconcentration system to determine Pb(II) and Cd(II) ions from aqueous solutions by flame atomic absorption spectrometric method. For this purpose, a novel metal complexing ligand thiazolidine carrying poly(hydroxyethylmethacrylate), PHEMA, microbeads were prepared. The effect of various experimental conditions on the adsorption and desorption properties of thiazolidine-immobilized pHEMA microbeads for Pb(II) and Cd(II) ions were investigated by applying batch and continuous column techniques. In order to optimize the conditions in the batch system, the effect of pH, adsorption equilibrium time and initial metal ion concentration were investigated. The maximum adsorption capacities of the thiazolidine-immobilized pHEMA microbeads were found as 69.62 mg g^{-1} for Pb(II) and 44.62 mg g^{-1} for Cd(II). Desorption of the adsorbed metal ion was realized using a 0.005 M HCl solution and desorption ratios greater than 98%. Adsorption-desorption cycles showed the feasibility of repeated use, at least, three times, of the sorbent system. The on-line continuous flow system was made up of a peristaltic pump, one four way valve, and a minicolumn (70 x 9 mm i.d.) (packed with thiazolidine immobilized pHEMA microbeads) coupled to flame atomic absorption spectrometer. The continuous flow system was optimized by using the univariate method in order to determine best chemical and flow conditions for the specified metal ions with good sensibility. Using optimized conditions, preconcentration factors were found 29 and 21 for Pb(II) and Cd(II), respectively; and the limits of detection were 11.2 μg L^{-1} Pb(II) and 5.6 μg L^{-1} Cd(II). The accuracy of the system was checked with tap water samples spiked with known amounts of metal ions.

Key Words: Pb(II), Cd(II), FAAS, on-line preconcentration, thiazolidine, pHEMA

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ÖZET

Sunulan bu çalışmada, alevli atomik absorpsiyon spektrometresi kullanılarak sulu çözeltilerde Pb(II) ve Cd(II) iyonlarının tayininde, basit bir sürekli önderiştirme sisteminin geliştirilmesi amaç edinilmiştir. Bu amaç için, metal kompleksleştirici yeni bir ligand olan thiazolidin bağlı poli(hidroksietilmetakrilat), pHEMA, mikroküreler hazırlanmıştır. Thiazolidin-immobilize pHEMA mikrokürelerin, Pb(II) ve Cd(II) iyonları için, adsorpsiyon ve desorpsiyon özelliklerine etki eden çeşitli deneysel parametreler kesikli ve sürekli kolon sistemi teknikleri uygulanarak incelenmiştir. Kesikli sistemde, optimum koşulların sağlanması amacı ile, pH etkisi, adsorpsiyon denge zamanı ve metal iyonu başlangıç derişimi değişkenleri incelenmiştir. Thiazolidin immobilize pHEMA mikrokürelerin adsorpsiyon kapasitesi Pb(II) iyonu için 69.62 mg g^{-1} ve Cd(II) iyonu için 44.62 mg g^{-1} bulunmuştur. Adsorplanmış metal iyonlarının desorpsiyonu 0.05 M HCl çözeltisi kullanılarak gerçekleştirilmiştir ve %98'den daha büyük desorpsiyon oranlarına ulaşılmıştır. Ard arda en az üç kez uygulanan adsorpsiyon-desorpsiyon döngüleri sorbentin tekrar tekrar kullanıma uygun olduğunu göstermiştir. Geliştirilen sürekli önderiştirme sistemi bir peristaltik pompa, dört yollu vana ve tiazolidin immobilize edilmiş pHEMA mikrokürelerle doldurulmuş 0.9 cm iç çaplı 7.0 cm uzunluğunda bir minikolon'dan oluşturulmuştur. Adsorpsiyon ve desorpsiyona etki eden kimyasal ve akış değişkenleri incelenmiş ve optimum koşullar belirlendikten sonra, Pb(II) ve Cd(II) iyonları için önderiştirme faktörleri sırasıyla 29 ve 21, gözlenebilirlik sınırları ise sırasıyla 11.2 μg L^{-1} ve 5.6 μg L^{-1} olarak bulunmuştur. Yöntemin doğruluğu referans çözelti ile yapılan deneyler sonucunda kanıtlanmıştır.

Anahtar Kelimeler: Pb(II), Cd(II), AAS, önderiştirme, thiazolidin, pHEMA

Danışman: Prof. Dr. Sema BEKTAŞ, Hacettepe Üniversitesi, Kimya Bölümü, Analitik Kimya Anabilim Dalı

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1. INTRODUCTION

The presence of heavy metals in the environment is a cause of concern due to their acute and long term toxicity. Cadmium and lead can be taken into the body through the pulmonary system from contaminated air or cigarette smoke or via the digestive system through water or food contamination from metal plant uptake (Yost, 1986). Cadmium can cause problems such as hypertension, emphysema, renal cancer, breast cancer, prostate cancer and kidney disease (Friberg et al., 1979). Lead has a great affinity to certain radicals and functional groups, such as -SH and $-NH_2$. Lead is a metabolic poison and enzyme inhibitor. It can cause mental retardation and semipermanent brain damage in young children. Lead has the ability to replace calcium in the bone to form sites for long term release (Stokinger, 1981).

In order to detect the usually low lead and cadmium concentrations, very sensitive techniques are required. Although flame or electrothermal atomic absorption spectrometry or inductively coupled plasma emission spectrometry have sufficiently low limits of detection, trace analysis is often hindered by severe matrix effects. Therefore it is necessary to employ preconcentration and separation techniques to enrich the analyte and solve the matrix problems. Most of the work on matrix separation and analyte preconcentration applied complexing agents containing imidoacetate or oxine functional groups immobilized on several supports, such as polystyrene, divinylbenzene, glass of controlled porosity, carboxymethylcellulose, etc. (Chandler et al., 1997).

Packed column on-line preconcentration and seperation coupled with spectroscopic techniques has been shown to be very effective in enhancing the sensitivity and selectivity of trace metals in samples with complex matrices. These techniques require low consumption of reagents, sample and time, involve less risk of sample contamination and loss, increased sampling frequency and throughput as well as ease of automation. Most studies have used micro or minicolumn packed with various sorbents to meet all the analytical needs for extraction as well as separation of the analyte of interest.

The present study aims to developed a simple on-line preconcentration system for the determination of trace amounts of the Pb(II) and Cd(II) ions in flame atomic absorption spectrometry (FAAS). Preconcentration was based on the chemical sorption of Pb(II) and Cd(II) ions onto a mini-column packed with thiazolidine carrying poly(hydroxyethylmethacrylate), pHEMA, microbeads.

The present work was organized in three main parts. In the first part of the study, pHEMA microbeads was synthesized by a suspension polymerization technique and then thiazolidine was immobilized onto pHEMA microbeads. The characterization of thiazolidine incorporated microbeads was realized using Fourier Transform Infrared Spectroscopy (FTIR) and elemental analysis and swelling test techniques. In the second part of the study, adsorption and desorption of Pb(II) and Cd(II) ions from aqueous solutions onto the thiazolidine immobilized pHEMA microbeads was investigated in batch processes. In the last part of the study, on-line preconcentration system was applied to preconcentrate the Pb(II) and Cd(II) ions from aqueous solutions to determine the trace amounts of these ions. The continuous preconcentration-elution system consists of a peristaltic pump and a minicolumn with an inner diameter of 0.9 cm and packed with dried thiazolidine-immobilized microbeads. In the preconcentration step, aqueous solutions containing small amounts of heavy metal ions were continuously pumped through the column for a certain time. Then the metal ions were retained on the minicolumn was eluted with a suitable elution solution. The concentration of metal ions in the eluent was determined by a flame atomic absorption spectrometer. The continuous flow system was optimized by using the univariate method in order to determine best chemical and flow conditions for the specified metal ions with good sensibility.

This approach for the preconcentration and determination of heavy metal ions by using on-line preconcentration system has many advantages than batch/manual procedures that all samples and standards are subjected to exactly the same treatment from the moment of injection to the moment of detection and that the same column is used for all samples and standards.

2. THEORETICAL

2.1. Preconcentration of Metal Ions

The determination of trace levels of metal ions in various samples usually requires a preconcentration step and/or separation of the analyte from the matrix before the instrumental analysis. There are, at present, two principle methods of preconcentration, off- and on-line procedures. With off-line preconcentration, the enrichment manifold is completely separated from the measurement instrument, and all chemical preconcentrations are conducted independently away from the spectrometer. In the second procedure, the enrichment manifold is connected directly to the spectrometer and the preconcentration and measurement can not be considered as two separate techniques, as the specific instrumentation performs the chemical pre-treatment of the sample and detection of the analyte.

The separation of the metal ions from the liquid sample in both of these methods can be obtained in several ways, however, one of the most commonly used approaches consist of allowing the sample to flow through a column packed with an active material that is capable of retaining the analyte. The selective retention of metal ions can be obtained by two different procedures: (1) a ligand, which can interact with the analytes, is added to the sample; the resulting complex species are then retained by the stationary phase of the column, (2) the complexing ligand is immobilized on the stationary phase, which then systematically retains the metal ions as the sample flows through the column in an ion-exchange fashion.

Both of these techniques have found widespread application in off- and on-line modes as they can provide the necessary detection power, in particular for the case of sea-water analysis. Sturgeon and co-workers used 8-hydroxyquinoline or diethyldithiocarbamate and C_{18} silica in an off-line system for the determination of various metal ions in sea-water (Sturgeon et al., 1982) . Ruzicka and Arndal demonstrated the possibility of using the

same ligands and a solid substrate in an on-line system, with excellent results (Ruzicka and Arndal, 1989).

The simplest on-line preconcentration system consists of a pump, which is used to propel the carrier stream through a narrow tube; a four-way-valve or an injection port; and a minireactor in which the sample zone disperses and reacts with the components of the carrier stream. In such a system each sampling cycle consist of two separate operations: preconcentration and elution. First, a large sample volume (e.g., 5 mL) is injected, within typically 1 minute, through an adsorptive column. Then a small volume of eluting reagent (e.g., 50 μL) is injected liberating the 100 times preconcentrated analyte into the spectrometer.

The main advantage of using on-line preconcentration is that all samples and standards are subjected to exactly the same treatment from the moment of injection to the moment of detection and that the same column is used for all samples and standards. The advantages of the system can be summarized as,

- low consumption of reagents, sample and time
- less risk of sample contamination and loss
- higher efficiency and better reproducibility than batch/manual procedures.

2.2. Some Applications of Off- and On-Line Preconcentration with Atomic Spectrometry

In the literature, different off- and on-line preconcentration systems to determine trace amounts of metal ions have been reported. Porta et al. used an on-line preconcentration method utilizing a microcolumn of XAD-2 resin functionalized with 1-(2-thiazolyazo)-2-naphthol (Porta et.al., 1992). They used this resin to preconcentrate Cd, Cu, Fe, Mn, Ni and Zn from river water and Antarctic sea-water prior to their determination by inductively coupled plasma atomic emission spectrometry. They used 2 mol dm^{-3} HCl + 0.1 mol dm^{-3} HNO_3 for the elution of the metal ions retained on the column. They obtained for preconcentration factor of 125 for injection time of 5 min. The

detection limits were 2 ng L^{-1} for Mn and 40 ng L^{-1} for Ni. Ferreira et al. used a minicolumn packed with Amberlite XAD-2 resin loaded with calmagite reagent for preconcentration and determination of copper by flame atomic absorption spectrometry (Ferreire et.al., 2000). To optimize the system, they studied the effect of the sample pH, the concentration of the eluent, the effect of the sample and eluent flow rate and the influence of electrolytes on copper sorption. They obtained a preconcentration factor of 32 in 13.5 mL of sample solution. Table 2.1 shows the determination of copper in several commercial food samples using the proposed methodology.

Table 2. 1. Copper determination in several commercial food samples - (Ferreire et al., 2000).

Sample	Copper Added, (μgL^{-1})	Copper Found, (μgL^{-1})	Recovery,%
Rice Flour Brand 1	0.00	1.19 ± 0.1	-
	1.00	2.12 ± 0.2	95.0
	2.00	3.16 ± 0.1	98.5
Rice Flour Brand 2	0.00	1.20 ± 0.2	-
	1.00	2.15 ± 0.1	99.0
	2.00	3.62 ± 0.2	91.5

The direct determination of trace metals in seawater by electrothermal atomic absorption spectrometry (ETAAS) is difficult even with sophisticated background correction and chemical modification; not only because of the presence of many trace metals at concentrations near or below the detection limit, but also because the sea-water matrix may cause serious interference. Preconcentration procedures can solve the above two problems and allow easy determination. Chang et al., applied an on-line preconcentration system to determine Cd, Co and Ni in sea-water by electrothermal atomic absorption spectrometry (Chang et.al., 1999). Retention of the metal ions as a complex on the microcolumn (2.5 cm x 0,94 mm i.d.) was achieved by using Muromac A-1 as the chelating resin; 20% HNO_3 was then used for elution. Detection limits (and sample volumes) were 1.2×10^{-4} $\mu g\ L^{-1}$ for Cd (400 μL), 0.007 $\mu g\ L^{-1}$ for Co (1800 μL) and 0.033 $\mu g\ L^{-1}$ for Ni (800 μL). These detection limits refer to preconcentration of an aliquot of sea-water blank based on three times the standard deviation of eight replicate measurements. In

another study, Xu et al., applied a sequential injection system for on-line sorbent extraction preconcentration of trace amounts of cadmium in electrothermal atomic absorption spectrometry (Xu et.al., 2000). They used a microcolumn packed with C_{18} for sorption of the cadmium pyrolidinedithiocarbamate complex and achieved an enrichment factor of 19. Farzanch and Akhavi studied the off-line preconcentration of trace cadmium from water samples for a flame atomic absorption spectrometry determination (Farzanch and Akhavi, 2001). They used a minicolumn (9 cm x 13 mm i.d.) loaded with alumina modified with 1-(2-pyridylazo)-2-naphthol (PAN). A sample solution up to 1000 mL containing μg Cd at pH 10.2 was passed through a microcolumn packed with 1.5 g sorbent at a flow rate of 5 mL min^{-1}. They used 10 mL of 2 M nitric acid solution for desorption of cadmium collected on the column. They achieved a preconcentration factor of 100 by passing 1000 mL of sample through the microcolumn. The detection limit calculated was 24.3 ng mL. They applied the method to the determination of Cd in waste, tap and mineral waters (Table 2.2).

Table 2. 2. Analytic recovery of cadmium added to some water samples (Farzaneh and Akhavi, 2001).

Sample	Cd added (μg L^{-1})	Found (μg L^{-1})
Tap water	20	19.80 ± 1.51
Mineral water	20	20.12 ± 2.20
Waste water	0	8.56 ± 0.52
Waste water	10	18.47 ± 0.30

Tewari and Singh used off-line preconcentration system with a minicolumn packed with Amberlite XAD-2 and Amberlite XAD-7 based chelating resins for lead determination by flame atomic absorption spectrometry (Tewari and Singh, 2002). They reported that, all resins quantitatively sorb Pb(II) at pH 3.0 – 8.0 when the flow rate is maintained between 2 and 10 mL min^{-1} and HNO_3 (0.5 – 4 M) instantaneously elutes Pb(II) from all chelating resins. They achieved the sorption capacities in the range of 16.0 – 186.0 μmol g^{-1} and loading half-time between 3.2 and 15.5 min. They found limit of detections of 2.44 ng mL^{-1} and 2.76 ng mL^{-1}, for Amberlite XAD-2 and Amberlite XAD-7,

respectively. Sperling et.al. developed flow injection on-line column separation and preconcentration ETAAS system for the fully automated determination of ng L^{-1} amounts of lead (Sperling et al., 1996). They used a microcolumn packed with Pb-O2 macrocycle immobilized silica gel. They obtained a collection efficiency of 77% and with a sample loading flow rate of 3 mL $min.^{-1}$ for a 60 seconds preconcentration time, the enrichment factor was 77 and the throughput was 17 samples per hour. They found 2.7% relative standard deviation (n =10) at the 300 ng L^{-1} level, and the detection limit (3σ) was 0.4 ng L^{-1}. Dressler et al. studied on determination of Cu, As, Se, Cd, In, Hg, Tl, Pb and Bi in waters and in biological materials by inductively coupled plasma mass spectrometry, after an on-line separation (Dressler et al., 1998). They used a minicolumn which contained about 30 mg of C_{18} immobilized on silica and the salts of dithiophosphoric acid O,O-diethyl ester (DDTP) as a complexing agent for the matrix separation and preconcentration of analytes. They used methanol as eluent. They obtained preconcentration factors in the range of 5 to 61, depending on the analyte and the limits of detection varied from 0.43 ng L^{-1} for Bi to 33 ng L^{-1} for Cu (Table 2.3).

Biurrun et al. developed an on-line preconcentration technique for flow-injection flame atomic absorption spectrometry for the determination of trace metals in natural waters (Biurrun et al., 1995). They used a minicolumn (20 mm X 2 mm i.d.) filled with a poly(aminophosphonic acid) chelating resin (PAPhA, 20 – 30 mesh) for the preconcentration procedure and 3 mol L^{-1} HCl for the elution. They achieved detection limits of 0.5, 5.0, 1.5, 1.6, 3.5, 0.6, 3.2, 3.1 and 0.4 μg L^{-1} for Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, respectively.

Table 2. 3. Figures of merit of the proposed method (Dressler et al., 1998).

Metal	Parameters		
	LD, ng L^{-1}	Enrichment factor	RSD, %
Cu	2.2	22.1	4.6
As(III)	5.1	27.1	3.6
Se(IV)	6.6	1.3	4.2
Cd	6.7	19.1	4.4
Tl	0.79	5.1	3.5
In	14.6	9.1	4.9
Hg	4.8	16.1	2.8
Pb	4.5	22.1	4.3
Bi	0.43	20.1	5.5

Dominguez et al. investigated the determination of trace and ultratrace amounts of cadmium in mussels by FAAS with preconcentration on a chelating resin in a flow injection system (Dominguez et al., 1998). They used a minicolumn (85 x 1.6 mm i.d.) packed with PAPhA resin for preconcentration of cadmium and used dilute HCl for elution. They achieved a preconcentration factor of 16 – 47, equivalent to 3.4 – 10 mL sample, by using a time-based technique. They found detection a limit of 0.56 μg L^{-1} for 3.4 mL of sample. Colognesi et al. evaluated the preconcentration and recovery of lead and cadmium traces at ng L^{-1} level in standard solutions and natural aqueous samples using a graphite furnace atomic absorption spectrometry (Colognesi et al., 1997). They used a micro-conic column and 1,2-dihydroxy-3,5-benzendisulphonic acid on a macroporous anion-exchange resin for preconcentration of Pb and Cd ions. They used 0.1 mol L^{-1} HCl for the recovery of the analytes. They obtained the detection limits 9 and 7 ng L^{-1} for Pb and Cd respsectively. Giacomelli et.al. proposed an automated flow injection system for the preconcentration of Bi and Pb from acid solutions of alloys and determination by electrothermal atomic absorption spectrometry (Giacomelli et.al., 2000). They used a minicolumn filled with activated carbon for preconcentration of Bi(III) and Pb(II) after complexation with the amonium salt of DDTP. They used ethanol as the eluent. They analyzed four certified

steel samples and a non-certified aluminum foil, spiked with the analytes. Their results are given in table 2.4 and table 2.5.

Table 2. 4. Analytical results for Bi and Pb in certified reference steels (n = 3) (Giacomelli et.al., 2000).

Sample	Bi		Pb	
	Reference ($\mu g\ g^{-1}$)	Determined (µg g-1)	Certified (µg g-1)	Determined (µg g-1)
SRM 361	4.0	4.3 ± 0.2	0.25 ± 0.05	0.21 ± 0.04
SRM 362	20.0	22.0 ± 0.9	4.8 ± 0.5	5.1 ± 0.9
SRM 363	8.0	7.5 ± 0.8	18.6 ± 0.5	17 ± 2
SRM 364	9.0	9.2 ± 0.4	230 ± 5	220 ± 11

Table 2. 5. Recovery test for Bi and Pb in an aluminum foil solution (n = 3) (Giacomelli et al., 2000).

Sample	Added concentration ($\mu g\ L^{-1}$)	Bi		Pb	
		Obtained concentration ($\mu g\ L^{-1}$)	Recovery (%)	Obtained concentration ($\mu g\ L^{-1}$)	Recovery (%)
1	1.0	0.96 ± 0.06	96	1.1 ± 0.2	110
2	1.0	1.1 ± 0.2	110	1.05 ± 0.05	105
3	2.5	2.2 ± 0.2	88	2.6 ± 0.5	104

2.3. CHELATING POLYMERS

Chelating polymer resin materials are mainly used in analytical, industrial and radiochemical laboratories, but only to a limited extent in solving environmental problems. Metal pollution of the environment poses unique problems. Predominantly, metal pollution originates with trace contamination in waters and soil systems. The behavior of trace metals in the environment is primarily determined by the specific forms of the metals rather than by their bulk concentrations. Since metals are not subject to biodegradation, for practical purposes they have infinite lifetimes. The most promising way to decontaminate aqueous systems such as wastewater treatment sludges and

recover the trace metals from them is by employing specific chelating resin materials. Although almost all common chelating polymers are non-selective, research efforts are being directed to synthesize selective chelating polymers with high physical and chemical stability, for metal extraction.

2.3.1. General Properties

The chemistry underlying the use of ion-exchange and chelating polymers for the separation and preconcentration of trace elements is reasonably well understood and progress today is mainly improving the specificity of the resins and the techniques of application. The analytical application of chelating polymers depend on many factors. Normally a metal ion exists in natural water as a hydrated ion or as a complex species in association with various anions, with little or no tendency to transfer to a chelating polymer. To convert a metal ion into an extractable species, its charge must be neutralized and some or all of its water of hydration replaced. The nature of the metal species is therefore of fundamental importance in extraction systems. Most significant is the nature of the functional group and/or donor atom capable of forming complexes with the metal ions in solution, and it is logical to classify chelating polymers on this basis. Also, for simplicity, it is desirable to classify chelating polymers according to Figure 2.1. This method of classification is not meant to imply that these systems are mutually exclusive. Indeed, some polymers can belong to more than one class, depending on experimental conditions.

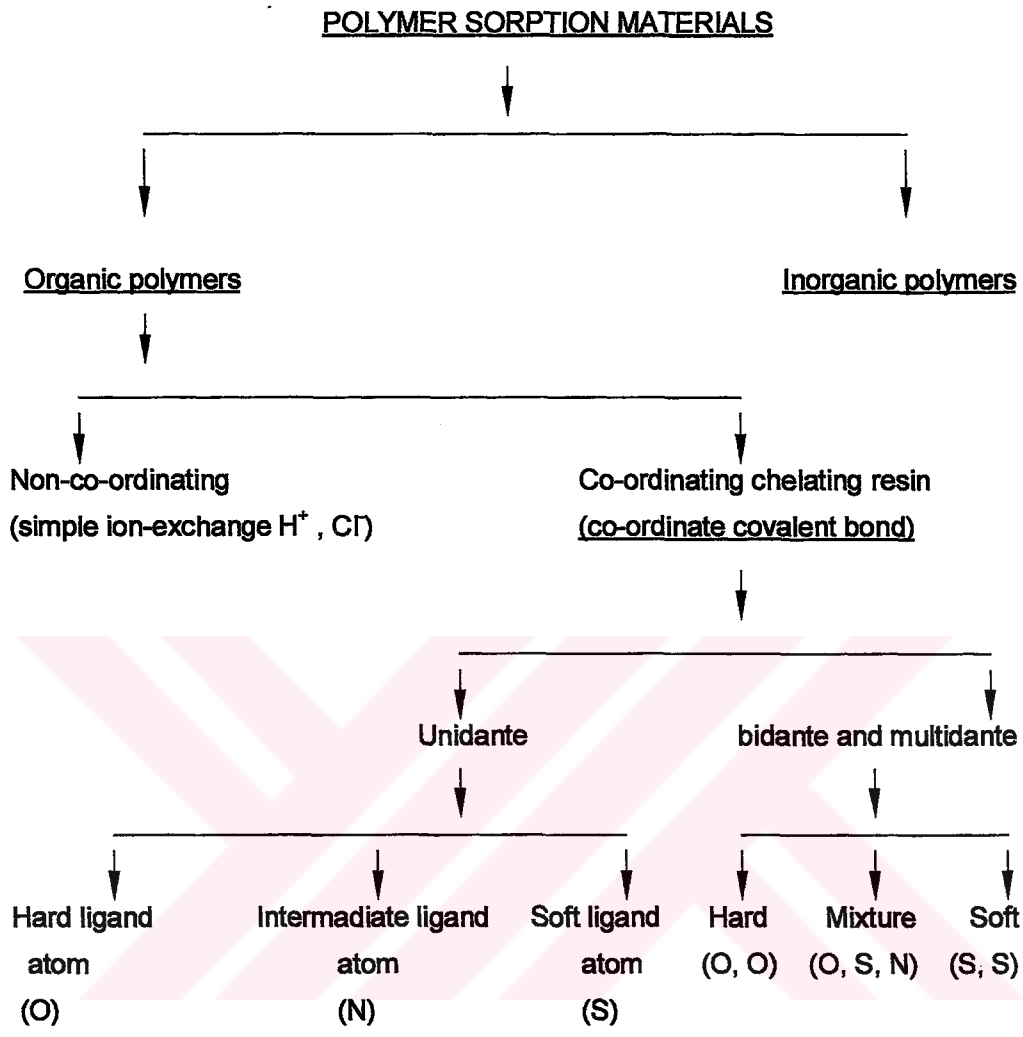

Figure 2.1. Classification of chelating polymers

2.3.2. Functional Groups

The functional group atoms capable of forming chelate rings usually include oxygen, nitrogen and sulphur. Nitrogen can be present in a primary, secondary or tertiary amine, nitro, nitroso, azo, diazo, nitrile, amide, and other groups. Oxygen is usually in the form of phenolic, carbonyl, carboxylic, hydroxyl, ether, phosphoryl, and some other groups. Sulphur is in the form of thiol, thioether, thiocarbamate, disulphide groups.

These groups can be introduced into the polymer by chemical transformation of the matrix or by the synthesis of sorbents from monomeric ligands. The insertion of suitable specific functional groups into the polymeric matrix makes them capable of reacting with metal ions or metal species under certain favourable conditions, to form chelate rings. The selective concentration and separation of elements from natural water systems depends both on elemental speciation and the chelating properties of the polymer.

2.3.3. Selection of chelating polymers

Synthetic chelating polymers have almost entirely displaced inorganic ion exchange polymers, with a few exceptions such as metal phosphates (zirconium and stannic phosphates) and some oxides (MnO_2, Al_2O_3, SiO_2 gel).

Conventionally, the resin materials can be classified into three main divisions: (a) cation-exchangers, (b) anion-exchangers, and (c) chelating polymeric resins. These can further be subdivided into strong, weak, or intermediate types, depending on the functional group.

The choice of an effective chelating resin and its value in analytical method development is dictated by the physicochemical properties of the resin materials. These are the acid-base properties of the metal species and the resin materials, and the polarizability, selectivity, sorptive capacity, kinetic and stability characteristics of the resin. Chelating polymers usually contain polyfunctional groups. Akaiwa and Kawamoto have discussed the advantage of having asynergic agent on a chelating resin to improve the sensitivity and separation of trace metals (Akaiwa and Kawamoto, 1982). One of the rules of selection is based on the concept of hard and soft acids and bases. The functional groups in the chelating polymer materials usually act as bases; oxygen-containing functional groups are hard and sulphur-containing groups soft. Functional groups with a basic nitrogen atom have an intermediate character. Although this guide highly useful in practical selection and

synthesis of chelating polymers, it should be borne in mind that there is a substantial difference in the stability of complexes formed by metal ions with macromolecular and low molecular-weight functional ligands. This is primarily caused by the polymeric structure for the resin material.

The kinetic characteristics of a chelating polymer are of considerable importance and depend on the nature and properties of the polymeric matrix and the degree of cross-linkage. Whereas in the ordinary type of exchanger the exchange processes are more rapid and controlled mainly by diffusion, those in a chelating exchanger are slower and controlled either by a particle-diffusion mechanism or by a second-order chemical reaction. For complexation or sorption to occur, it is not sufficient that surface functional groups are present; they must also be accessible for the chelation of the metal ion without steric hindrance. Thus within chelating resin particles, many surface functional groups may remain inactive in complexation equilibrium can not be attained.

On comparing the kinetic properties of different chelating sorbents, it quickly becomes obvious that the sorbents with the best characteristics are those based on hydrophilic macro-porous co-polymers and cellulose, or on fibrous materials. Sorbents based on synthetic fibers are successfully used for various purposes.

Preconcentration with chelating sorbents improves the sensitivity and reliability of determination of elements in a wide variety of sampples, including natural waters, geological, biological and industrial materials.

2.4. Polymerization Techniques

The main polymerization techniques are bulk, solution, suspension and emulsion polymerizations. Plasma polymerization and gas phase polymerization are other possibilities for polymerization. To produce spherical beads, emulsion or suspension or dispersion polymerization is performed. The size of resulting beads is less then 1 μm and ranges from 100 μm to 5 mm, if emulsion or suspension technique is followed, respectively. Suspension polymerization proceeds by dispersing the monomer in water with a suspending agent and then converting the dispersed droplets into polymer by reaction with an initiator that is normally soluble in the monomer.

The monomer droplets are usually more finely dispersed in emulsion polymerization, with diameters ranging from a few microns to >10 μm. Unlike suspension polymerization, the emulsion process does not simply involve polymerization of the monomer droplets. Nucleation and growth of smaller particle is a significant mechanism in emulsion polymerization (Billmeyer 1971).

Suspension polymerization technique is a conventional technique to produce polymers in bead form in large quantities for industrial applications. In this technique, the monomer phase is broken into droplets (a few microns in a diameter) within a dispersion medium (usually an aqueous phase), and stabilized by a surfactant dissolved in dispersion medium. These monomer droplets containing a monomer phase soluble initiator are then individually polymerized by applying a temperature/agitation program. This technique is usually used for the production of spherical polymeric particles between about 50 and 1000 μm. A wide particle size distribution is usually observed because of inherent size distribution in the mechanical homogenization (agitation) step and because of a coalescence problem that arises in this type of polymerization (Pişkin et al., 1994).

2.5. ATOMIC ABSORPTION SPECTROMETRY

Atomic Absorption Spectrometry (AAS) is the measurement of the absorption of optical radiation by atoms in the gaseous state.

2.5.1. Instrumentation

The general construction of an atomic absorption spectrometer is simple and is shown schematically in Figure 2.2. The most important components are a radiation source, which emits the spectrum of the analyte element; an atomizer, such as a flame, in which the atoms of the sample to be analyzed are formed; a monochromator for the spectral dispersion of the radiation with an exit slit for selection of the resonance line; a detector permitting measurement of radiation intensity, followed by an amplifier and a readout device that presents a reading.

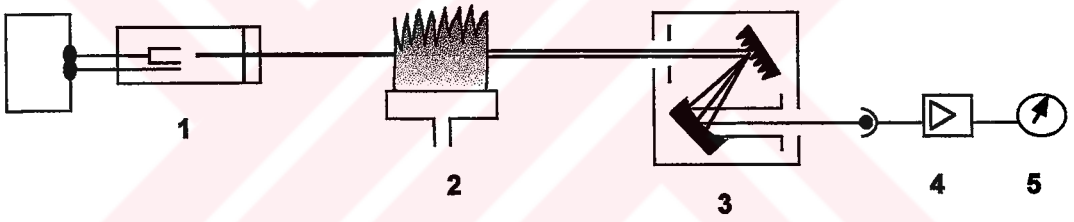

Figure 2.2. Schematic construction of an atomic absorption spectrometer.
1 Radiation source, 2 Flame, 3 Monochromator, 4 Detector,
5 Electrical measuring system with readout device.

2.5.1.1. Radiation Sources

Since atoms are only able to absorb radiation within a very narrow frequency interval, certain demands must be placed upon the radiation source. Although continuum radiation sources afford a high total illumination intensity, the illumination intensity in the interval of interest of about 0.0005 nm to 0.005 nm is nevertheless too weak. For this reason the radiation source used for absorption measurements should emit the spectrum of the element to be determined.

The most common source for atomic absorption measurements is the *hollow cathode lamp*. A hollow cathode lamp consist of a glass cylinder filled with an

inert gas (argon or neon) under a pressure of several hundred pascal (a few Torr) into which an anode and a cathode have been fused. The cathode is generally in the form of a hollow cylinder and is either made of the analyte metal or filled with it. The anode is in the form of a thick wire, usually of tungsten or nickel.

If a voltage of several hundred volts is applied across the electrodes, a glow discharge takes place. If the cathode consist of two parallel electrodes or of a hollow cylinder, under suitable conditions the discharge occurs almost completely within the cathode, where two processes then take place. A stream of positive ions, generated from the carrier gas by the discharge, strikes the surface of the cathode and atoms of the cathode material are released by the collisions. These atoms pass into the region of the intense discharge where they meet a concentrated stream of gas ions and excited noble gas atoms and are hence excited to radiate their spectral lines. Since the majority of the radiation is emitted from within the cathode, the resultant beam is relatively well bundled.

The efficiency of the hollow cathode lamp depends upon its geometry and the operating potential. High potentials, and thus high currents, lead to greater intensities. This advantage is offset somewhat by an increase in Doppler broadening of the emission lines. Furthermore, the greater currents result in an increase in the number of unexcited atoms in the cloud; the unexcited atoms, in turn, are capable of absorbing the radiation emitted by the excited ones. This self-absorption leads to lowered intensities, particularly at the center of the emission band.

Electrodeless discharge lamps are useful sources of atomic line spectra and provide radiant intensities that are usually one to two orders magnitude greater than their hollow-cathode counterparts. A typical lamp is constructed from a sealed quartz tube containing a few torr of an inert gas such as argon and a small quantity of the metal (or its salt) whose spectrum is of interest. The lamp contains no electrode but instead is energized by an intense field of radio-frequency or microwave radiation. Ionization of the argon occurs to give

ions that are accelerated by the high frequency component of the field until they gain sufficient energy to excite the atoms of the metal whose spectrum is sought.

2.5.1.2. Atomizers

The emission spectrum of the analyte element emitted from the radiation source is passed through an "absorption cell" in which a portion of the incident radiation is absorbed by atoms produced by thermal dissociation, for example. Accordingly, the most important function of this absorption cell is to produce analyte atoms in the ground state from the ions or molecules present in the sample. This is without doubt the most difficult and critical process within the whole atomic absorption procedure. The success or failure of a determination is virtually dependent upon the effectiveness of the atomization; the sensitivity of the determination is directly proportional to the degree of atomization of the analyte element in the sample.

The Flame Technique

In flame atomization, a solution of the sample is sprayed into a flame by means of a nebulizer, which converts the sample solution into a mist made up of tiny liquid droplets. A complex set of interconnected processes then occurs; these processes ultimately lead to a mixture of analyte atoms, analyte ions, sample molecules, oxide molecules of the analyte, and undoubtedly a variety of other atomic and molecular species formed by reactions among the fuel, the oxidant, and the sample. With so many complex processes occurring, it is not surprising that atomization is the most critical step in flame spectroscopy and the one that limits the precision of such methods.

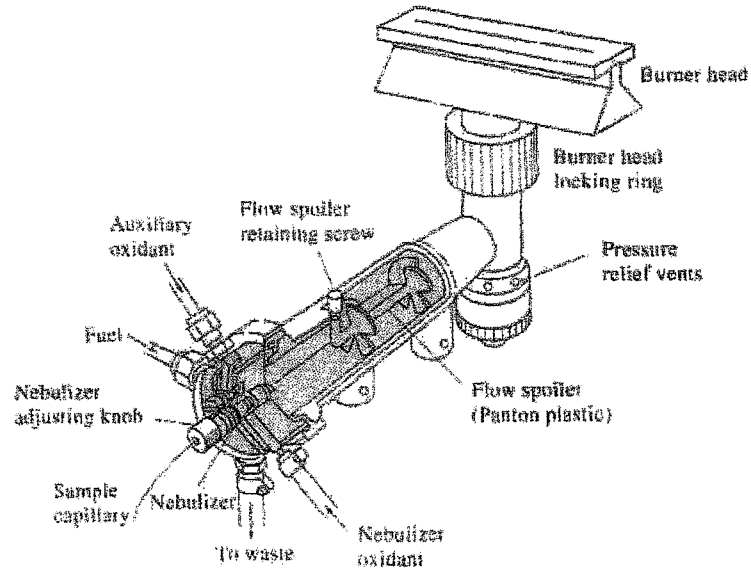

Figure 2.3. A laminar flow burner.

Figure 2.3. is a diagram of a typical commercial laminar flow burner that employs a concentric tube nebulizer. The aerosol is mixed with fuel and flows past a series of baffles that remove all but the finest droplets. As a result of the baffles, the majority of the sample collects in the bottom of the mixing chamber, where it is drained to a waste container. The aerosol, fuel and oxidant are then directed into a slotted burner, which provides a flame that is usually 5 or 10 cm in length. Laminar flow burners provide a relatively quite flame and a long path length. These properties tend to enhance sensitivity and reproducibility.

Table 2.6. lists the common fuels and oxidants employed in flame spectroscopy and the approximate range of temperatures realized with each of these mixtures. The burning velocities listed in the fourth column of the table are of considerable importance, because flames are stable in certain ranges of flow rates only. If the flow rate does not exceed the burning velocity, the flame propagates itself back into the burner, giving flashback. As the flow rate increases, the flame rises until it reaches a point above the burner where the flow velocity and the burning velocity are equal. This region is where the flame is stable. At higher flow rates, the flame rises and eventually reaches a point where it blows off of the burner. Clearly, the flow

rate of the fuel/oxidant mixture is an important variable that has to be closely controlled.

Table 2.6. Properties of flames

Fuel	Oxidant	Temperatures,°C	Burning Velocity cm s^{-1}
Natural gas	Air	1700 - 1900	39 - 43
Natural gas	Oxygen	2700 - 2900	379 - 390
Hydrogen	Air	2000 - 2100	300 - 440
Hydrogen	Oxygen	2550 - 2700	900 - 1400
Acetylene	Air	2100 - 2400	158 - 266
Acetylene	Oxygen	3050 - 3150	1100 - 2480
Acetylene	Nitrous oxide	2600 - 2800	285

Electrothermal Atomizers

Electrothermal atomizers generally provide enhanced sensitivity because the entire sample is atomized in a short period, and the average residence time of the atoms in the optical path is a second or more.

In electrothermal atomizers, a few microliters of sample are first evaporated at low temperature and then ashed at a somewhat higher temperature in an electrically heated graphite tube or cup. After ashing, the current is rapidly increased to several hundred amperes, which causes the temperature to soar to perhaps 2000°C to 3000°C; atomization of the sample occurs in a period of a few milliseconds to seconds. Figure 2.4.(a) is a cross sectional view of a commercial electrothermal atomizer. Atomization occurs in a cylindrical graphite tube, which is open at both ends and has a central hole for introduction of sample by means of a micropipet. The tube is about 5 cm long and has an internal diameter of somewhat less than 1 cm. The interchangeable graphite tube fits snugly into a pair of cylindrical graphite electrical contacts located at the two ends of the tube. These contacts are held in a water-cooled metal housing. Two inert gas streas are provided. The external stream prevents the entrance of outside air and a consequent incineration of the tube. The internal stream flows into the two ends of the

tube and out the central sample port. This stream not only excludes air but also serves to carry away vapors generated from the sample matrix during the first two heating stages.

Figure 2.4.(b) illustrates the L'vov platform, which is often used in graphite furnaces such as that shown in (a). The platform is also graphite and is located beneath sample entrance port. The sample is evaporated and ashed on this platform in the usual way. When the tube temperature is raised rapidly, however, atomization is delayed since the sample is no longer located directly on the furnace wall. As a consequence, atomization occurs in an environment in which the temperature is not changing so rapidly. More reproducible peaks are obtained as a consequence.Table 2.7 lists the properties of both flame and electrothermal atomizers.

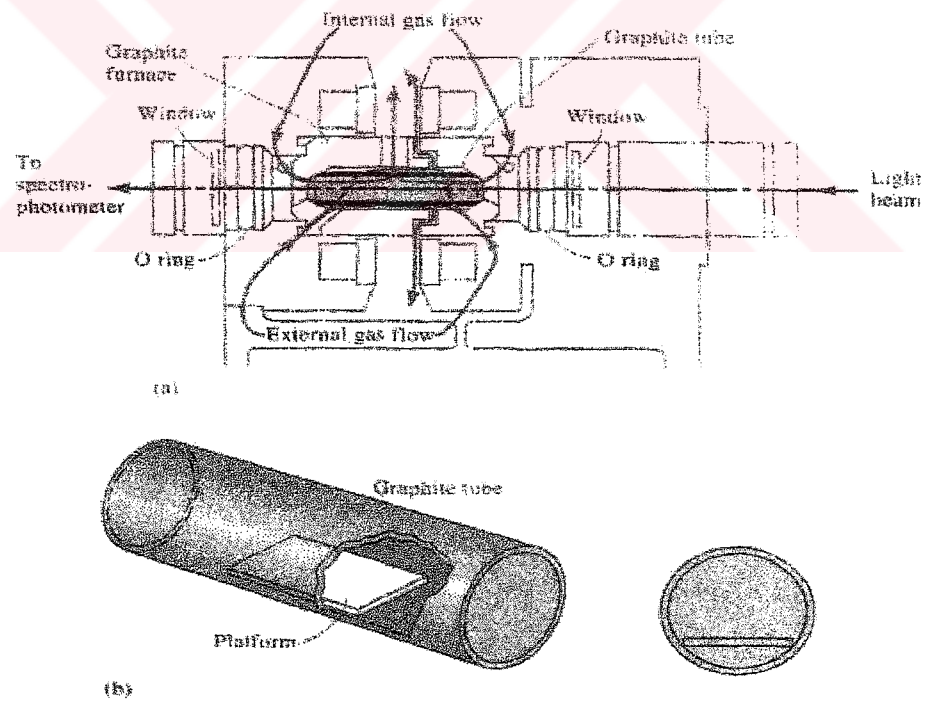

Figure 2.4. (a) A cross-sectional view of a graphite furnace. (b) The L'vov platform and its position in the ggraphite furnace.

Table 2.7. Advantages and disadvantages of both flame and electrothermal atomizers.

AAS Atomization Method	Advantages	Disadvantages
Flame	*Faster than furnace methods *Results are highly reproducible	*Handles only liquid samples *Flame is a source of noise *Wastes sample solution *Residance time of atoms in optical path of flame is very small
Graphite Furnace	*Handles smaller sample sizes *Handles solid and liquid samples *Higher sensitivity *Low amounts of noise from the furnace *Lower detection limits for many elements *Sample solution is not wasted	*Much more time consuming *More severe matrix effects *Lower precision *Analytical range is low compared to flame & plasma atomization *Analysis is usually limited to metals

2.5.1.3. Optics

The spectral range of interest for atomic absorption spectrometry begins in the near infrared at 852.1 nm, the wavelength of cesium, and reaches down into the vacuum UV below 200 nm. Atomic absorption spectrometry therefore covers much the same wavelength range that is of interest for atomic emission spectrometry or UV/VIS spectrometry. In principle it should then be possible to employ proven monochromators in atomic absorption. However, it has been shown that the requirements in AAS with respect to resolution and dispersion of the monochromator are different from those of other techniques. One of the greatest advantages of atomic absorption spectrometry, namely its specificity, is based on the use of element-specific radiation sources that emit the spectrum of the analyte element in the form of very narrow spectral lines. While the quality of an instrument in other spectrometric techniques frequently depends on the resolution of the monochromator or on its spectral bandpass, the range of radiation that passes through the exit slit, these factors are not of primary importance in AAS. The monochromator in an atomic absorption spectrometer has the sole

task of separating the resonance line of the analyte element from other emission lines of the source. Prisms and gratings serve to disperse the radiation into individual wavelengths.

2.5.1.4. Detectors

Photomultipliers are mainly used in atomic absorption spectrometry to convert optical radiation into an electrical signal. They consist of a vacuum photocell with an anode, a radiation sensitive electrode (photocathode), and a number of emission cathodes (dynodes) which have increasing positive potential with respect to the photocathode.

A photoelectron released from the photocathode is attracted to the first dynode and falls upon it with a kinetic energy that is proportional to the voltage gradient. It then releases a number of secondary electrons which are accelerated and for their part release an even greater number of electrons, and so on, so that the effect is still further amplified. The amplification of a photomultiplier is dependent upon the applied high voltage. This can have values up to 1000 V to 1500 V.

2.5.2. Interferences in Atomic Absorption Spectrometry

The presence of other constituents accompanying the analyte element in the sample can lead to interferences, which can cause systematic errors in the determination. The influence of the atomizing medium, such as the flame, graphite material, or quartz cell, or of the solvent is not regarded as an interference since sample and reference solutions are affected to equal degrees. An interference will cause an error in the analytical result only if the interference is not adequately accounted for in the evaluation procedure.

In spectrochemical analysis, interferences are generally divided into two classes: Spectral interferences and non-spectral interferences.

2.5.2.1. Spectral Interferences

Spectral interferences are caused by the incomplete isolation of the radiation absorbed by the analyte element from other radiation or radiation absorption due to, or affected by, the interferent. Spectral interferences can arise from:

♦ Absorption of the source radiation by overlapping atomic lines or molecular bands of the concomitants.

♦ Scattering of the source radiation on non-volatilized particles from concomitants.

♦The indirect influence of concomitants on the blank background absorption or scattering of the atomizer

♦By absorption of foreign radiation if, in addition to the analytical line, the source emits further radiation within the spectral bandpass of the monochromator. This effect is observed particularly when a continuum source is used.

Several methods have been developed for correcting for interferences;

*The two line correction method

*The continuous-source correction method

*Background correction based on the Zeeman effect

*Background correction based on source self-reversal

Figure 2. 5. illustrates a second method, the continuous-source correction method, for background corrections that is widely used. Here a deuterium lamp provides a source of continuous radiation throughout the ultraviolet region. The configuration of the chopper is such that radiation from the continuous source and the hollow cathode lamp are passed through the atomizer. The absorbance of the deuterium radiation is then subtracted from that of the analyte beam. The slit width is kept sufficiently wide so that the fraction of the continuous source that is absorbed by the atoms of the sample is negligible. Therefore, the attenuation of its power during passage through the atomized sample reflects only the broad-band absorption or scattering by the sample matrix components. A background correction is thus achieved

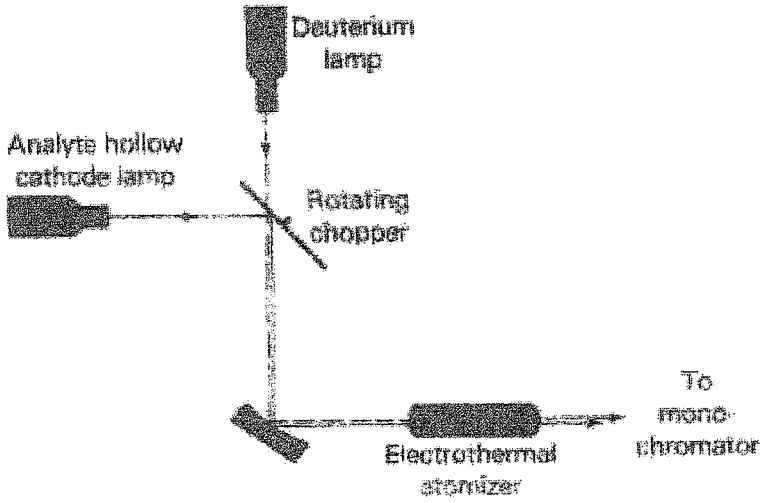

Figure 2.5. Schematic of a continuous source background correction system.

2.4.2.2. Non-Spectral Interferences

Non-spectral or chemical interferences result from various chemical process occuring during atomization that the analyte signal is affected directly. Perhaps the most common type of interference is by anion, which form compounds of low volatility with the analyte and thus reduce the rate at which it is atomized. Interference due to formation of species of low volatility can often be eliminated or moderated but use of higher temperatures. Alternatively, releasing agent, which are cations that react preferentially with the interference and prevents its interaction with the analyte, can be employed. Protective agents prevent interference by forming stable but volatile species with the analyte. An ionization buffer is added to suppress ionization. By adding an easily ionized element, such as cesium or potassium, the concentration of the free electrons in the absorption volume is increased substantially, thereby suppressing and stabilizing ionization of the analyte.

3. EXPERIMENTAL

3.1. Preparation of Polyhydroxyethylmethacrylate (pHEMA) Microbeads

3.1.1. Materials

Thiazolidine was supplied from Sigma (St. Louis, MO, USA) and used as received. 2-Hydroxyethylmethacrylate (HEMA) was purchased from Sigma (St. Louis, MO, USA) and was purified by vacuum distillation under a nitrogen atmosphere and stored at 4°C until use. The comonomer ethyleneglycoldimethacrylate, (EGDMA) (Merck, Darmstadt, Germany) was used as the crosslinking agent. The polymerization initiator 2,2'-azobisisobutyronitrile (AIBN) was provided from Fluka Switzerland. The dispersion medium was a saturated aqueous solution of magnesium oxide (MgO) (Sigma).

3.1.2. Polymerization method

pHEMA microbeads were prepared by a suspension polymerization technique (Denizli and Pişkin, 1995). Polymerization was carried out in an aqueous dispersion medium containing magnesium oxide which was used to decrease the solubility of the HEMA in the medium. The monomer phase containing HEMA,EGDMA and AIBN was added to the dispersion medium within a laboratory type reactor (i.e., a two-neck flask with a volume of 500 mL) provided with a blade type stirrer (Figure 3.1.). In order to produce polymeric microbeads of about 200 μm in a diameter and with a narrow size distribution, the HEMA/EGDMA ratio, the monomer phase/dispersion phase ratio, the amounts of EGDMA and AIBN, and the agitation speed were 1:3 (v/v), 1:10 (v/v) 0,33 (mol EGDMA/MOL HEMA), 0.0015 (mol AIBN/mol HEMA), 600 rpm, respectively. Polymerization was carried out at 70 °C for 3 h and then at 90°C for 1 h. After cooling, the polymeric microbeads were separated from the polymerization medium and residual MgO was removed by washing a dilute HCl solution. The microbeads were also washed with water and ethanol, and then dried in a vacuum desiccator at room temperature.

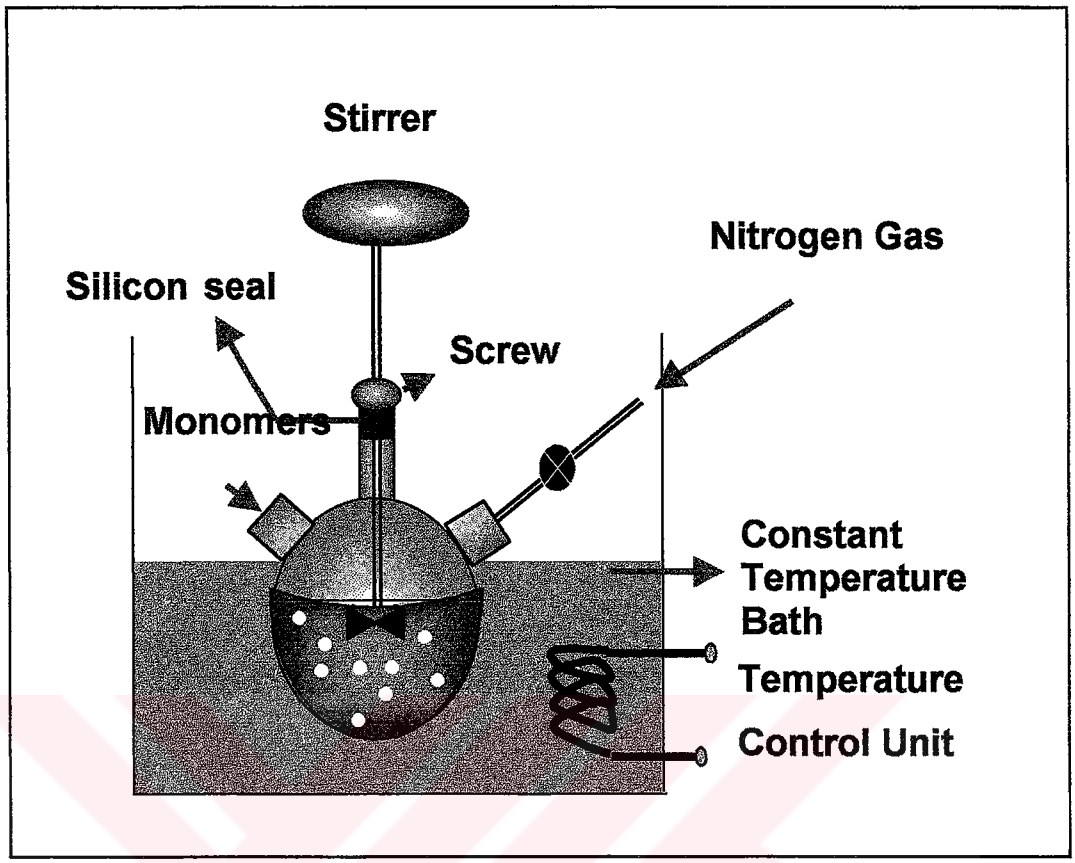

Figure 3.1. Schematic representation of polymerization system used in the preparation of pHEMA microbeads.

3.1.3. Thiazolidine immobilization

Thiazolidine was covalently immobilized onto the pHEMA microbeads. The immobilization reaction is shown in Figure 3.2. Briefly, 1.0 g of thiazolidine were dissolved in tetrahydrofuran and 0,5 g of NaH was added to his solution. The nucleophilic substitution reaction was started by adding 10 g of dry pHEMA microbeads. The reaction was carried out at a constant temperature of 40°C for 24 h. Thiazolidine-incorporated microbeads were first filtered, and then washed with distilled water and methanol several times until all the physically adsorbed and/or absorbed thiazolidine molecules were removed.

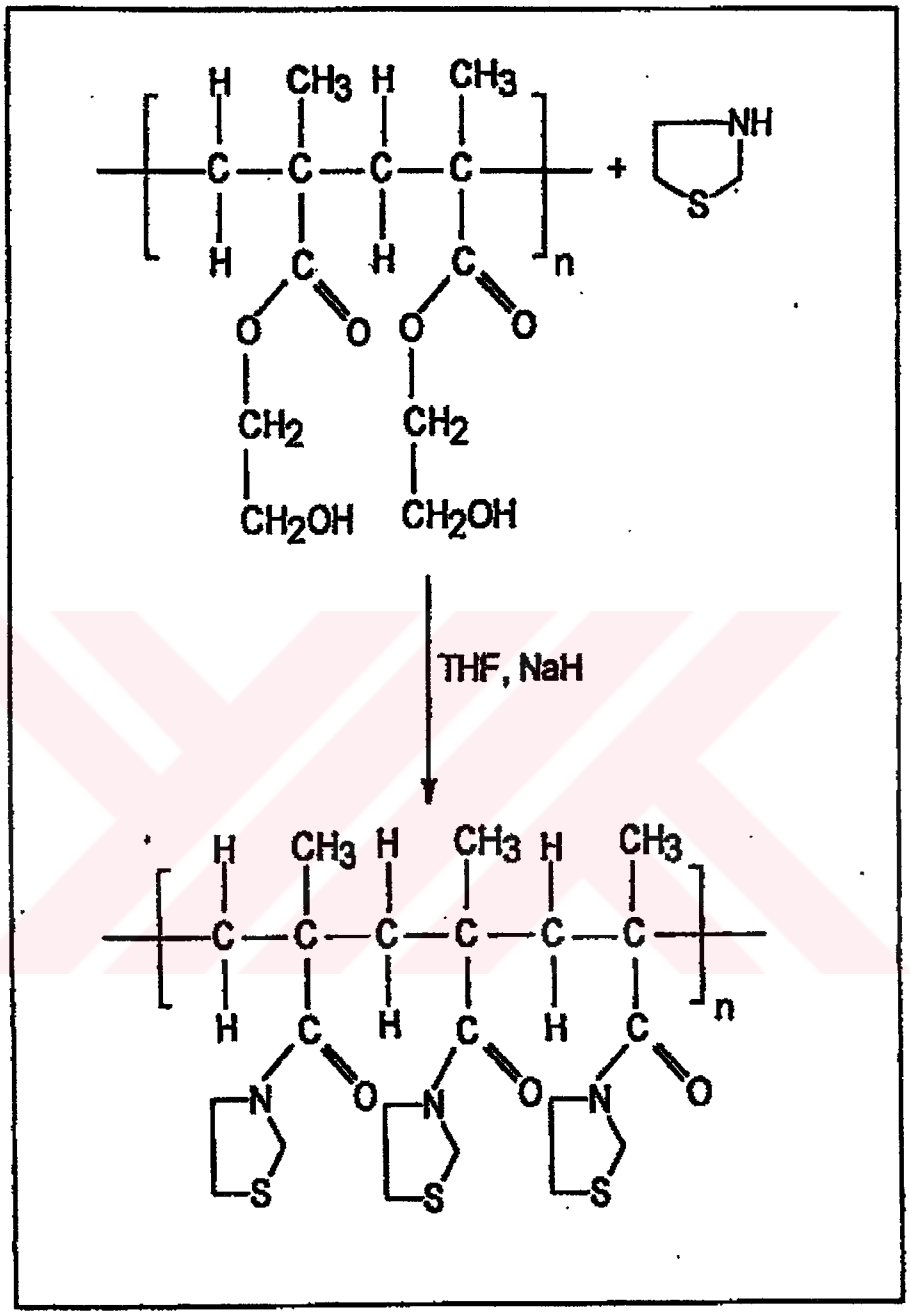

Figure 3.2. Coupling of thiazolidine onto the pHEMA microbeads.

3.1.4. Characterisation of pHEMA microbeads

3.1.4.1. Swelling studies

To determine the equilibrium water swelling ratio of pHEMA microbeads, approximately 3.0 g of dry polymer sample were put into a cylindirical tube. The height of the bed formed by the dry microbeads (H_d) was measured. Then , 50 mL of buffer solution at a certain pH and ionic strength was added into the tube. The sealed tube was shaken on a rotater with 30 rpm for 24 h. at the end of this period; the height of the bed formed by swollen pHEMA microbeads (H_s) was recorded. The equilibrium water swelling ratio was calculated based on the following expression:

$$\text{Equilibrium Water Swelling Ratio} = (H_s / H_d)x100 \qquad (3.1)$$

3.1.4.2. Elemental Analysis

To evaluate the degree of thiazolidine incorporation the synthesized pHEMA-thiazolidine microbeads were subjected to elemental analysis using a Leco Elemental Analyzer (Model CHNS-932).

3.1.4.3. FTIR Studies

FTIR spectra of the pHEMA and pHEMA-thiazolidine microbeads were obtained by using a FTIR spectrophotometer (FTIR 8000 Series, Shimadzu, Japan). The dry microbeads (about 0.005 g) was thoroughly mixed with KBR (0.1 g, IR Grade, Merck, Germany) and pressed into a pellet and the FTIR spectrum was then recorded.

3.2. Heavy Metal Adsorption/Desorption in Batch System and On-line Preconcentration System

3.2.1. Reagents and Apparatus

All chemicals were of analytical-reagent grade. A standard solutions of 1000 mg L^{-1} Cd(II) and 1000 mg L^{-1} Pb(II) were prepared from $Cd(NO_3)_2.4H_2O$ and $Pb(NO_3)_2$ (Merck) in deionized water, respectively. From this solutions, other dilute standard solutions were prepared daily. De-ionized water of 18.2 MΩ cm resistivity obtained from a Milli-Q water purification system (Millipore) served for preparation of all solutions. Hydrochloric acid (Jansen-Chimica, 37%) and pure sodium hydroxide pellets (Merck) was used to adjust the sample pH.

A Shimadzu Model AA-6800 Flame Atomic Absorption Spectrophotometer equipped with deuterium lamp background correction was employed. The working conditions are given in Table 3.1.

Table 3.1. Working conditions.

Element	Wavelength	Bandwith	HCL current	Flame Composition	
				Acetylene	Air
Cd(II)	228.8 nm	0.5 nm	8 mA	1.8 L/min	13.5 L/min
Pb(II)	283.3 nm	0.5 nm	10 mA	2.0 L/min	13.5 L/min

The flow system comprised of an PETEC/Perimax 12 peristaltic pump (Germany) furnished with Tygon tubes. All connections were made by using fittings, unions and tees made of plastic and PEEK materials.

Continuous flow system

A schematic diagram of the flow system used for preconcentration and determination of lead and cadmium is shown in Figure 3.3. The flow system was made up of a peristaltic pump fitted with Tygon tubes, one four –way

valve and a minicolumn (70 mm x 9 mm i.d.) packed with thiazolidine immobilized poly(HEMA) microbeads. The metal ion solution was pumped through the column that contained the adsorbent and the remaining solution was discharged. Then, hydrochloric acid was pumped through the column for displacement of metal ions and the eluate was taken direct to the nebulizer-burner system of the flame atomic absorption spectrometer.

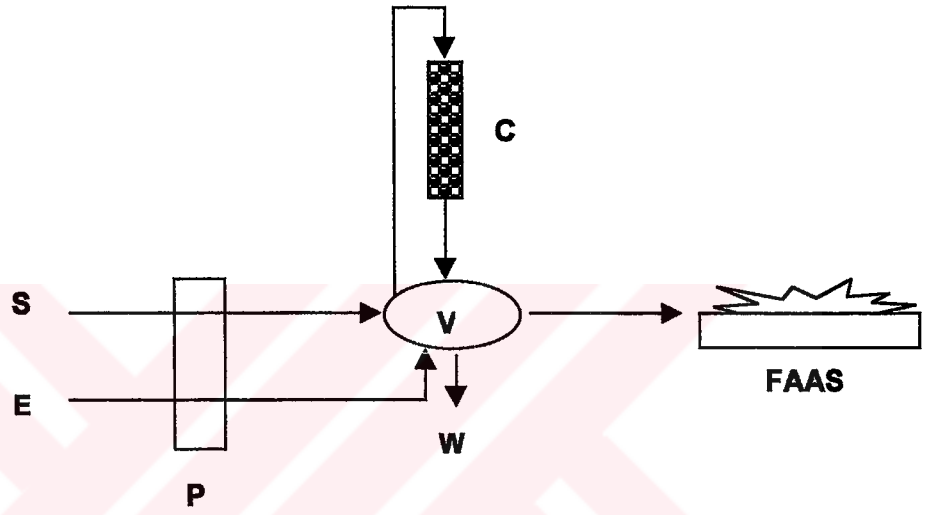

Figure 3.3. Schematic diagram of continuous flow system. E: eluent; S: sample; V: four-way valve; W: waste; C: column.

3.2.2. Cd(II) and Pb(II) ions adsorption in batch system

In the first pat of the thesis, adsorption of Cd(II) and Pb(II) ions from aqueous solutions were studied in batch systems. Aqueous solutions (20 mL) containing different amounts of heavy-metal ions (10-600 mg L^{-1}) were incubated with 50 mg of the thiazolidine immobilized pHEMA samples at different pH values (in the range of 2.0-6.0, which was adjusted with HCl or NaOH at the beginning of the experiment and not controlled afterwards) at room temperature, in the flasks agitated magnetically at an agitation speed of 600 rpm. After the desired incubation periods (up to 60 minutes), the aqueous phases were separated from the polymers by centrifugation (4000 rpm for 10 minutes), and the concentrations of the metal ions in these phases were measured by using a Flame Atomic Absorption Spectrophotometer. The

quantities of metal ions adsorbed per unit mass of the polymer (mmol metal ions/g polymer) were calculated by using the following expression.

Metal ions adsorbed = $[(C_o-C)x\ V] / [m \times 1000]$ (3.2)

Here, C_o and C are the concentrations of the metal ions in the aqueous phase before and after the incubation period, respectively (mg L^{-1}); V is the volume of the aqueous phase (mL); and m is the amount of the polymer used (g).

Competitive heavy-metal adsorption from aqueous solutions containing Cd(II) and Pb(II) ions were investigated by following a similar procedure described above. These studies were performed at a constant pH: 6.0 and at 20°C.

3.2.3. Desorption and Reuse in batch system

Desorption of heavy-metal ions was achieved by using 20 mL of the eluent i.e., 0.05 M HCl. The polymer was loaded with the heavy-metal ions in the following conditions: initial concentration of the metal ions: 50 mg L^{-1} for Pb (II) and Cd (II); amount of the polymer: 50 mg; volume of the adsorption medium: 20 mL; temperature: 20°C; adsorption time: 30 minutes. Then, these polymers were placed in this desorption medium and stirred at a stirring rate of 600 rpm up to 30 minutes. The concentrations of the metal ions in the aqueous phase were measured as mentioned before. Desorption ratio was calculated from the following expression:

$$\text{Desorption ratio} = \frac{\text{Quantity of metal ions desorbed to the elution medium}}{\text{Quantity of metal ions adsorbed onto the sorbent}} \times 100$$

In order to obtain the reusability of thiazolidine attached-pHEMA, adsorption-desorption cycle was repeated three times by using the same sorbent. Adsorption conditions were as follows: initial concentration of the metal ions: 50 mgL^{-1} from the adsorption of single metal ion solutions, 80 mg L^{-1} from the adsorption of metal ion solution containing two metal ions (equal amounts of the metal ions were used); amount of the polymer: 50 mg; volume of the

adsorption medium: 20 mL; temperature: 20°C; adsorption time: 30 minutes. The polymers were washed several times with 0.05 M HCl and deionized water and reloaded.

3.2.4. On-line preconcentration system

The on-line preconcentration system used was shown schematically in Figure 3.3. The flow system was operated in a time-based mode. The continuous preconcentration-elution system consisted of a peristaltic pump, a four-way-valve and a minicolumn containing the chelating resin (70 mm x 9 mm i.d., packed with 0.2390 g of pHEMA-thiazolidine).

In the preconcentration step, the sample or standard containing between 0 and 100 $\mu g\ L^{-1}$ lead at pH 5.3 was continuously pumped at 5.0 mL min^{-1} percolated through the minicolumn that contained the solid sorbent for 20 min (sample volume 100 mL). Then Pb(II) ions were retained by chemical sorption on the minicolumn, and the sample matrix was sent to waste. By switching the valve blank carrier (deionized water) was pumped at 5.0 ml min^{-1} (equal to the FAAS aspiration flow rate) for 1 min and 0.1 mol L^{-1} hydrochloric acid that flowed at 5.0 mL min^{-1}, displaced the lead complex. This eluate was taken direct to the nebulizer-burner system of the flame atomic absorption spectropohtometer. Signals were measured as peak height by using an instrument software. At the end of each cycle the blank carrier was passed through the minicolumn in order to condition it for the following sample introduction. For the preconcentration of cadmium, the sample or standard containing between 0 and 10 $\mu g\ L^{-1}$ cadmium at pH 5.5 was continuously pumped through the minicolumn at 5.0 mL min^{-1}. The cadmium was retained on the minicolumn, and the sample matrix was sent to waste and the elution step, the same procedure, as mention above for lead, was applied.

4. RESULTS AND DISCUSSION

4.1. Characterization of pHEMA Microbeads

4.1.1. Swelling Properties

The pHEMA microbeads used in this study are cross-linked hydrophilic matrices, i.e., hydrogels, therefore, they do not dissolve in aqueous media, but do swell, depending on the degree of cross-linking ratio and on the hydrophilicity of the polymeric matrix. The equilibrium swelling ratio of the pHEMA-thiazolidine microbeads used in this study is 58%. Compared with pHEMA (55%), the water uptake ratio of the pHEMA-thiazolidine microbeads was increased. Several possible factors may contribute to this result. First, incorporating thiazolidine actually introduces more hydrophilic functional groups into the polymer chain, which can attract more water molecules into polymer matrices. Second, reaction of thiazolidine with HEMA could effectively decrease the molecular weight of the resulting polymer and reduce the crystallinity of the structure. Therefore, the water molecules penetrate into the entaglement polymer chains more easily, resulting in an improvement of polymer water uptake behavior in aqueous solutions. It should be noted that these hydrophilic microbeads are quite rigid, and strong enough due to highly cross-linked structure; therefore suitable for packed-bed column applications. The size range obtained from the optical micrographs is 150-200 μm (in swollen form).

4.1.2. Elemental Analysis

From the elemental analysis results, the amount of thiazolidine immobilized onto pHEMA microbeads was calculated as 0.318 mmol/g from the nitrogen and sulphur stoichiometry. Note that HEMA does not contain nitrogen or sulphur. This amount determined by elemental analysis comes only from immobilized thiazolidine groups into the polymeric structure.

4.1.3. FTIR Studies

The FTIR spectrum of pHEMA and thiazolidine immobilized pHEMA microbeads are shown in Figure 4.1. When they are compared it can be seen that the band at 1562 cm^{-1} is characteristic C-N stretching band (amide) due to thiazolidine bonded to pHEMA.

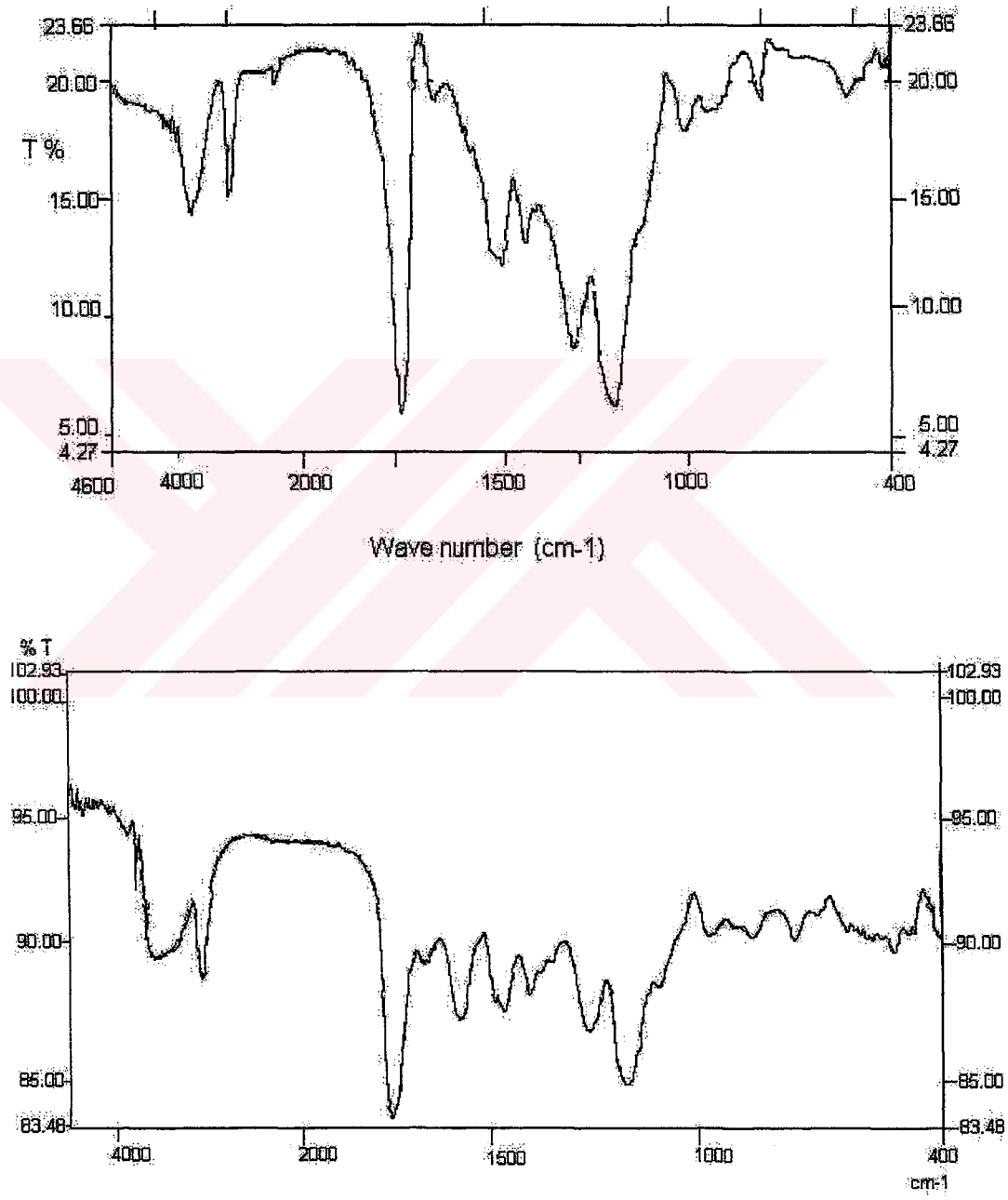

Figure 4.1. FTIR spectra of (a) pHEMA and (b) thiazolidine İmmobilized pHEMA microbeads.

4.2. Adorption/Desorption of Pb(II) and Cd(II) Ions in Batch System

4.2.1. Effect of pH

In most equilibria between metal ions and metal complexation ligands, the metal ions compete with protons for the binding sites on sorbents so that, as in almost all aqueous equilibria pH will be of dominant importance. The distribution of metal cations between free and bound states will depend on pH, and much less metal ion should bound under acidic conditions than at basic pH. Also, the extent of ionization of functional groups in sorbent is pH dependent, i.e., the carboxyl, hydroxyl and sulfhydryl groups are protonated at low pH values. Conversely, at higher pH the deprotonated groups (e.g., negatively charged thiols or carboxylate) will be more nucleophilic than the protonated species, therefore can form ion pairs or complexes with the metal ions (Der-Chyan and Srinivasan, 1996). Therefore, in this study, in order to establish the effect of pH on adsorption of metal ions onto the thiazolidine immobilized pHEMA, the equilibrium studies at pH values in the range 3.0-7.0 were investigated. For this purpose, 20 mL of each metal ion (40 mg L^{-1} for Pb(II) and Cd(II)) at different constant pH's were interacted with 0.05 g pHEMA-thiazolidine for 30 minutes. The pH values (3, 4, 5, 6, and 7) were chosen below 8 so that none of the metal hydroxides precipitated. The mixtures were filtered and washed with deionized water. Metal contents of the filtrates were determined by FAAS. Figure 4.2. shows the effect of pH on adsorption. A rapid increase in binding of lead and cadmium occurred between pH 3.0 – 5.0 and 3.0 – 6.0 respectively and reaching plateau values at around pH 5.0 for Pb(II) and 6.0 for Cd(II) .

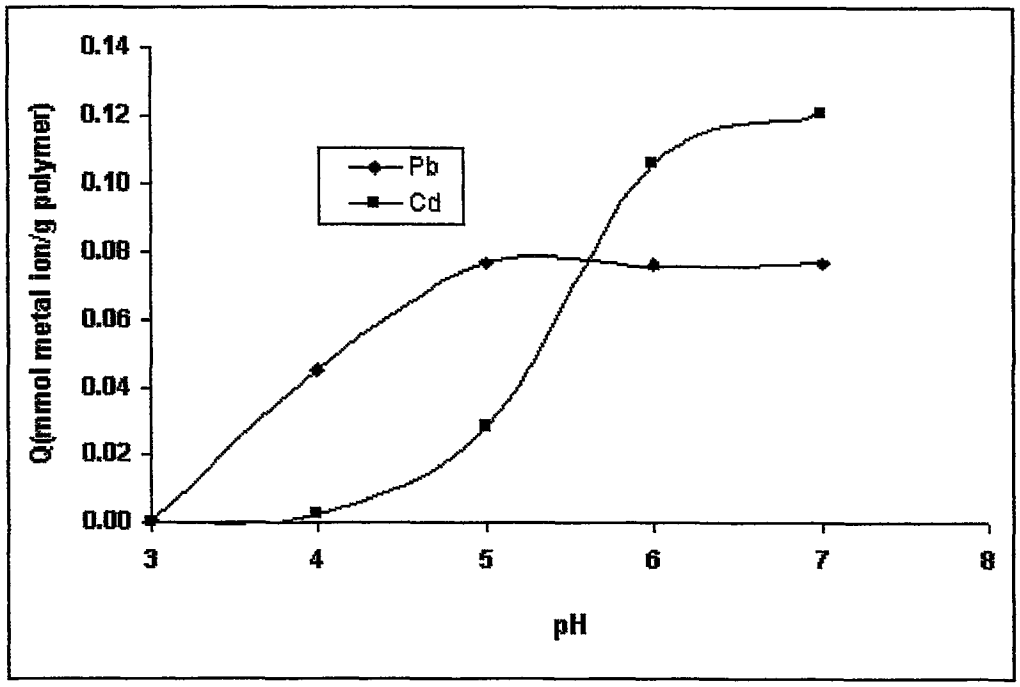

Figure 4.2. Effect of pH on the adsorption capacity of thiazolidine immobilized pHEMA for heavy metal ions. Adsorption conditions: initial concentration of metal ions: 40 mg L^{-1} for Cd(II) and Pb(II); amount of polymer: 50 mg; volume of adsorption medium: 20 mL; temperature 20°C; adsorption time 30 min.

4.2.2. Adsorption Rate

Figure 4.3 shows adsorption rates of Pb(II) and Cd(II) ions by thiazolidine attached pHEMA microbeads as a function of time. Note that these batch experiments were performed by using single (not mixed) solutions of the ions of interest. Figure 4.3 shows the changes in the amounts of metal ions adsorbed with time calculated by using Eq. (3.1). Adsorption conditions are given in the figure legend. The initial slopes of these curves reflect the adsorption rates. High adsorption rates are observed at the beginning, and then plateau values (i.e.,adsorption equilibrium) are gradually reached within 10 min for both metal ions.

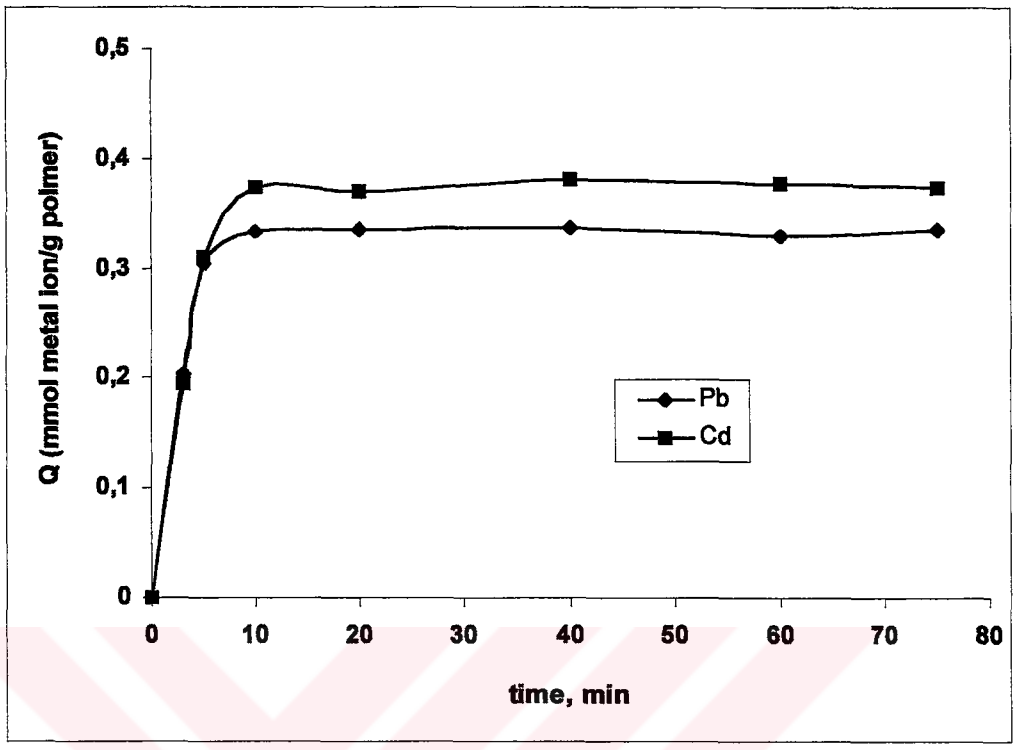

Figure 4.3. Adsorption rates of heavy metal ions by thiazolidine immobilized PHEMA. Adsorption conditions: initial concentration of metal ions: 500 mg L^{-1} for Cd(II) and 250 mg L^{-1} for Pb(II); pH:5.5; temperature 20°C.

Several experimental data on the adsorption kinetics of heavy metal ions by various sorbent have shown a wide range of adsorption rates. Roozemond et al. studied Cu and Cd uptake of 3,5-dimethyl-1-hydroxymethylpyrazole attached *p*-aminomethyl substituted poly(styrene-co-divinylbenzene) chelating polymer. They showed that adsorption is rather slow, after 2 days the resin appeared to reached equilibrium (Roozemond et al., 1988). Latha et al. studied ethylenediamine functionilized polyacrylamide resin for extraction of several metals such as Fe(III), Fe(II), Cu(II) and Ni(II) and they reported that complexation reaction proceeds very slowly (equilibrium time 5 h) (Latha et al., 1991). Ebraheem et al. studied divalent ions including Cd(II), Ni(II), Cu(II) and Zn(II) on phenol phenol formaldehyde polymer containing poly(salycyl aldoxime 3,5-dimethylene) and reported a 10 h equilibrium adsorption time (Ebraheem et al., 1997). Konishi et al. studied sorption of zinc, cadmium and lanthanum by biopolymer gel beads of alginic acid and they reported high adsorption rates, in which equilibrium was achieved in

about 2 h (Konishi et al., 1993). Arpa et al. studied Pb(II), Cd(II) and Cu(II) ions removal from aquatic systems using smectite. They reported high adsorption rates, in which equilibrium was achieved in 20 min (Arpa et al., 2001). In such an adsorption process, there are several parameters which determine the adsorption rate, such as agitation (or flow) rate in the aqueous phase, sorbent structural properties (e.g. size, porosity, surface area), amount of sorbent, metal ion properties (e.g. hydrated ionic radius), initial concentration of metal ions, pH, temperature, chelate-formation rate, and of course, existing of other ions which may compete with the ions of interest for active adsorption sites. All individual experimental studies published in the literature have been performed under different conditions; consequently it is not reasonable to make comparisions of the adsorptions rates reported.

4.2.3. Adsorption Capacity

To investigate the adsorption capacitiy of the thiazolidine attached pHEMA microbeads, 20 mL of each metal ion solution (pH adjusted to 5.5 for both lead and cadmium) at different initial concentrations were interacted with 0.05 g thiazolidine attached pHEMA microbeads for 30 min. The maximum initial concentration values were chosen as 300 mg L^{-1} for lead and 600 mg L^{-1} for cadmium so that none of the metal hydroxides precipitate. Heavy metal ion adsorption amounts of the thiazolidine attached pHEMA microbeads are presented as a function of the initial concentration of metal ions within the aqueous adsorption medium in Figure 4.4. This figure was prepared by using the plateau values of the adsorption rate curves. The amount of metal ions adsorbed per unit mass of the polymer increased with the initial concentration of metal ions, as expected. In order to reach the plateau values which represent saturation of the active sites (which are available for specific interaction with metal ions) on the sorbent, in other terms to obtain the adsorption capacities of the thiazolidine immobilized pHEMA for the interested metal ions, we increased the initial concentration of Pb(II) ions up to 300 mg L^{-1} and Cd(II) ions up to 600 mg L^{-1}. The adsorption capacities of the thiazolidine immobilized pHEMA microbeads are 0.336 mmol per gram of

the sorbent (69.62 mg g^{-1}) for Pb(II) and 0.397 mmol g^{-1} of the sorbent (44.62 mg g^{-1}) for Cd(II).

In the literature, a wide variety of sorbents with a wide range of adsorption capacities for heavy metal ions have been reported. Dev and Rao reported 0.460 mmol Cd(II)/g and 0.390 mmol Pb(II)/g adsorption capacity for poly-styrene-vinylbenzene macroreticular resin functionalized with bis-(N,N'-salicylidine)-1,3-propandiamine (Dev and Rao, 1996). Roozemond et al. showed an adsorption capacity of 0.355 mmol Cd(II)/g with pyrazole-containing poly(styrene-divinylbenzene) sorbents (Roozemond et al., 1988). Denizli et al. developed magnetic poly(methylmethacrylate) microspheres carrying ethylene diamine and they reported 0.162 mmol Cd(II)/g (Denizli et al., 2000). Arpa et al. used dye-affinity microspheres for heavy metal removal and they achieved 0.081 mmol g^{-1} and 0.075 mmol g^{-1} adsorption capacities for Pb(II) and Cd(II) ions, respectively (Arpa et al., 2001). Satıroglu et al. investigated competitive adsorption of heavy metal ions on monodisperse polystyrene microspheres carrying dithiocarbamate groups, and they reported adsorption capacity of 0.993 mmol Pb(II)/g and 1.121 mmol Cd(II)/g (Satıroglu et al., 1998). Murthy and Ryan found 0.034 – 0.128 mmol Cd(II)/g removal by cellulose-dithiocarbamate resins, (Murthy and Ryan, 1982). Liu et al. investigated Cd(II) adsorption onto the N-(hydroxymethyl)thioamide anchored macroretycular resin and they achieved 0.199 mmol g^{-1} adsorption capacity (Liu et al., 1998). Sarkar et al. used salicyl-aldoxime modified silica gel for recovery of Cu(II), Co(II), Ni(II), Zn(II), Fe(III) ions and they reported adsorption capacities in the range of 0.04 – 0.08 mmol g^{-1} (Sarkar et al., 1996). Comparing these data it seems that the adsorption capacities achieved with the thiazolidine immobilized pHEMA microbeads are very satisfactory.

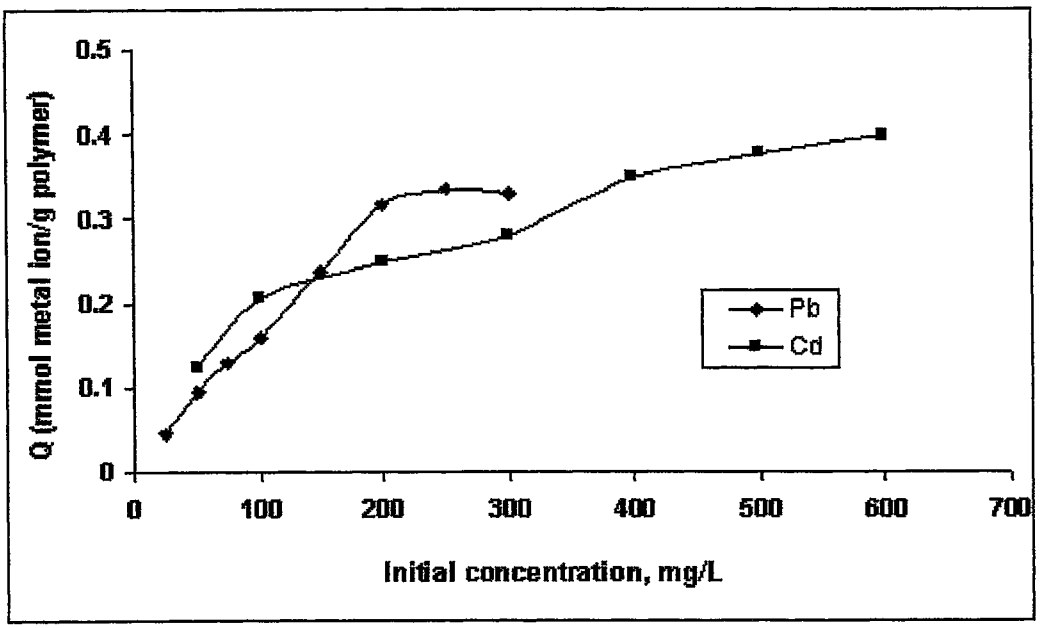

Figure 4. 4. Adsorption capacities of thiazolidine immobilized pHEMA microbeads for heavy metal ions. Adsorption conditions: amount of polymer, 50 mg; volume of the adsorption medium, 20 mL; pH 5.5; temperature 20°C; adsorption time, 60 min.

4.2.4. Competitive adsorption

In this group of experiments, competitive adsorption of Cd(II) and Pb(II) ions from solutions containing the ions together was investigated. Solutions (20 mL) containing 250 mg L^{-1} of metal ions were incubated with 50 mg of the thizolidine immobilized pHEMA microbeads for 30 min at pH 6.0, and at a temperature of 20°C. Table 4.2 gives the comparison of non-competitive and competitive adsorption of heavy metal ions on the thizolidine immobilized pHEMA microbeads. The adsorption amounts were 0.0356 mmol g^{-1} for Cd(II) and 0.326 mmol g^{-1} for Pb(II). It is clearly seen that immobilized thiazolidine ligand shows high affinity to Pb(II) ions. Cd(II) affinity of thiazolidine is almost negligible according to Pb(II) ions in competitive adsorption.

Table 4.1. Comparison of non-competitive and competitive adsorption amounts of heavy metal ions on the thiazolidine immobilized pHEMA microbeads.

Ion	Adsorption (mmol g^{-1})	
	Non-competitive	Competitive
Pb(II)	0.336	0.326
Cd(II)	0.397	0.0356

4.2.5. Desorption and reuse

To be useful in metal ion recycling processes, metal ions chelated should be easily desorbed under suitable conditions. Desorption of the adsorbed metal ions from the thiazolidine immobilized pHEMA microbeads was also studied in a batch experimental set-up. Desorption of metal ions from the loaded samples was realized using hydrochloric acid solution 30 minutes. of interaction time with 0.05 mol L^{-1} HCl is enough for complete desorption and the amounts of the stripping metal ions were almost the same with the sorbed amounts in the experimental error limits (Table 4.2.). In conclusion, when HCl is used as a desorption agent, the coordination spheres of chelated heavy metal ions is disrupted and subsequently metal ions are released from the solid surface into the desorption medium.

In order to ensure the reusability of the thiazolidine immobilized pHEMA microbeads, adsorption-desorption cycle was repeated three times using the same sorbent. Adsorption were achieved from the single metal ion solutions. The data are presented in Table 4.2. Resorption capacity of the sorbent for both metal ions did not change significantly during repeated adsorption-desorption operations.

Table 4.2. Reusability of the thiazolidine immobilized pHEMA microbeads; adsorption-desorption of metal ions from sorbent polymer[a].

Metal Ions	Metal ions adsorbed (μmol g^{-1} microbead)			Desorption ratio (%)		
	First	Second	Third	First	Second	Third
Cd(II)	205.0	198.9	194.9	98.9	98.6	98.2
Pb(II)	159.5	151.2	149.8	98.7	97.9	97.2

[a] Adsorption conditions: initial concentration of metal ions, 100 mg L^{-1}; amount of polymer, 50 mg; volume of adsorption medium, 20 mL; pH 5.5; temperature 20°C; adsorption time 60 min.; Desorption conditions: desorption medium, 0.05 mol L^{-1} HCl; volume of desorption medium, 20 mL; desorption time, 60 min.; temperature, 20°C.

4.3. Continuous Flow System Performance

The effect of column height and inner diameter on the preconcentration of lead and cadmium ions in the continuous flow system were examined. Three minicolumns were taken with heights 50, 70 and 120 mm, inner diameters of 2, 9 and 9 mm, packed with 0.08, 0.2 and 0.25 g of polymer. The results indicated that the small inner diameter of the column caused a problem in terms of sample flow resistance, due to swelling of the polymer, so back pressure within the column was observed. The other two columns (70 and 120 mm i.d.) did not cause any problems in terms of sample flow resistance; in these columns the flow decreased slowly, probably because of a long-term tightening of the resin bed. Increase in the height of the minicolumn scarcely decreased and broadened the observed signal. Therefore a minicolumn, 70 mm x 9 mm i.d., was chosen for further analyte preconcentration studies.

The continuous flow system was optimized by using the univariate method in order to determine the best chemical and flow conditions for lead and cadmium determination with good sensibility.

4.3.1. Effect of pH on adsorption

In order to evaluate the effect of pH on the lead and cadmium absorbance signal, the pH values of the sample solutions were adjusted to a range of 3.0-7.0 with HCl or NaOH. For this purpose, 100 $\mu g\ L^{-1}$ of Pb(II) and 10 $\mu g\ L^{-1}$ Cd(II) solution at different pH values was pumped through the column at a flow rate of 5.0 mL min^{-1} (at a pumping time of 20 min., 100 mL of sample). The results of the effect of pH on signal is shown in Figure 4.5. As can be seen from Figure 4.5, the maximum amounts of lead and cadmium adsorbed by thiazolidine immobilized pHEMA microbeads were at pH 5.3 and 5.6, respectively. Therefore, pH values 5.3 for lead and 5.6 for cadmium were selected for subsequent studies, considering that , at lower pH values, complexation and retention to be incomplete, and at higher values (especially at pH 6) the performance of the chelating polymer decreases rapidly.

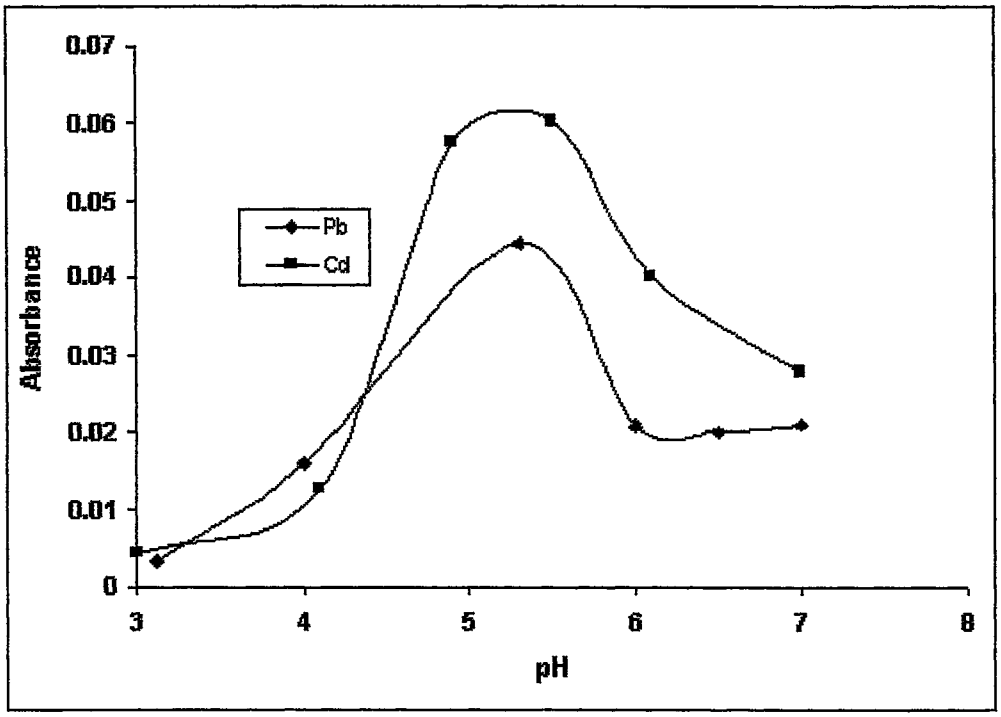

Figure 4.5. Effect of pH on the retention of Pb(II) and Cd(II) ions.

4.3.2. Effect of flow rate of sample solution

As the retention of elements on adsorbent depends upon the flow rate of the sample solution, its effect was examined under the optimum conditions (pH, eluent, etc.) by passing 100 mL of sample solution through the minicolumn with a peristaltic pump. The flow rates were adjusted in a range varying from 0.8 mL min^{-1} to 5.7 mL min^{-1}. As shown in Figure 4.6, the analytical signals obtained remained independent with increasing flow rates. These results were an indication of the fast adsorption kinetics for both of Pb(II) and Cd(II) adsorption. As mentioned in section 4.2.2., fast adsorption kinetics for both Pb(II) and Cd(II) adsorption on pHEMA-thiazolidine microbeads were also observed in batch experiments. It is well known that higher flow rates permit using high sample volumes which increases the preconcentration factor. Therefore a flow rate of 5.0 mL min^{-1} was chosen throughout the preconcentration studies.

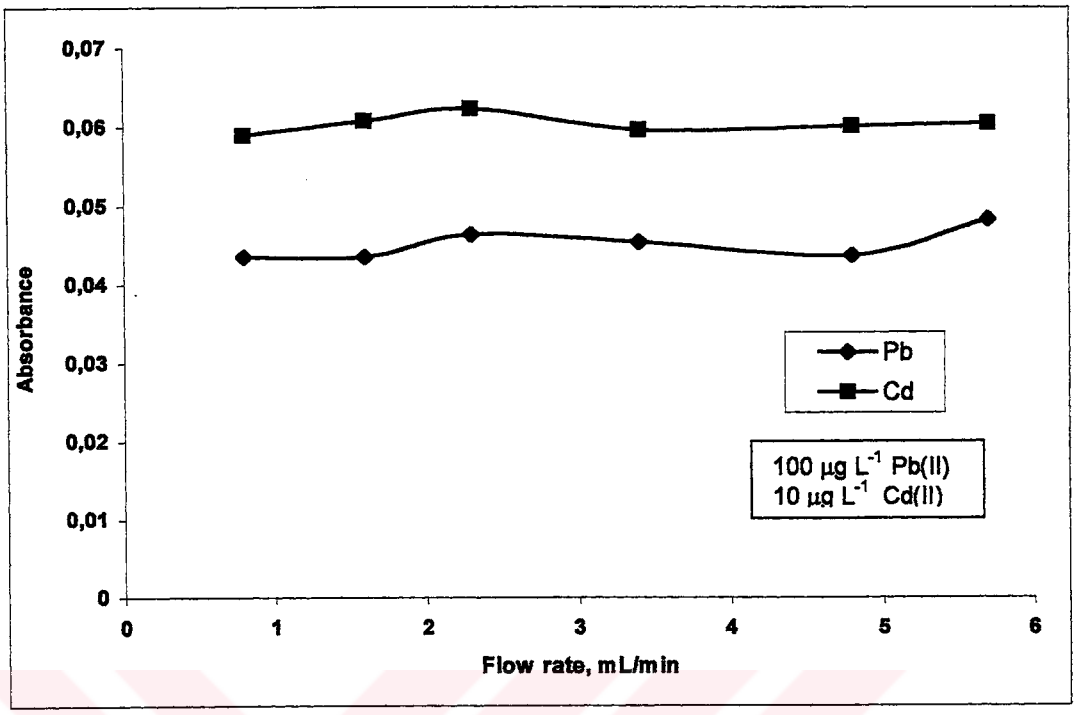

Figure 4.6. The effect of flow rate of sample solution on retention of Pb(II) and Cd(II) ions.

Ferreira et al. developed an on-line continuous flow system for copper enrichment and determination by FAAS (Ferreira et al., 2000). They used a minicolumn packed with Amberlite XAD-2 resin loaded with calmagite reagent for chemical sorption of Cu(II) ions. They investigated the sample flow rate in the range between 1.57 and 4.92 mL min^{-1}, and reported that the analytical signal increased slowly on decreasing flow rates, and copper sorption kinetics was not so fast. Biurrun et al. studied the determination of trace metals in natural waters by FAAS following on-line ion-exchange preconcentration (Biurrun et al., 1995). They reported that the absorbance signal as a function of the flow-rate reveals a maximum between 2.8 and 3.4 mL min^{-1}, and the signal was decreased dramatically at flow rates > 5 mL min^{-1} owing the very short residence times of the sample in the minicolumn. Chang et al. used a miniature column packed with Muromac A-1 chelating resin for determination of ultra-trace amounts of cadmium, cobalt and nickel in sea-water by ETAAS with on-line preconcentration (Chang et al., 1999) and reported a 3.5 µL s^{-1} sample flow rate. Farzaneh and Akhavi studied the preconcentration and determination of trace cadmium using PAN by FAAS

(Farzaneh and Akhavi). They showed that adsorption decreased with an increase in the sample flow rate when it is greater than 6 mL min^{-1}.

4.3.3. Effect of eluent concentration

The desorptions of lead and cadmium ions from the minicolumn were investigated by using various concentrations of hydrochloric acid solution. The concentration of the stripping agent was varied between 0.01 mol L^{-1} and 0.5 mol L^{-1}. The analyte was eluted from the minicolumn at a flow rate of 5.0 mL min^{-1}, after loading 100 mL of samples (100 μg L^{-1} Pb(II) and 10 μg L^{-1} Cd(II) ions solutions) that flowed at 5.0 mL min^{-1}. It was observed that the elution was complete at 0.05 mol L^{-1} HCl concentration (Figure 4.7). Accordingly 0.1 mol L^{-1} HCl solution was selected as eluent for lead and cadmium ions for further studies.

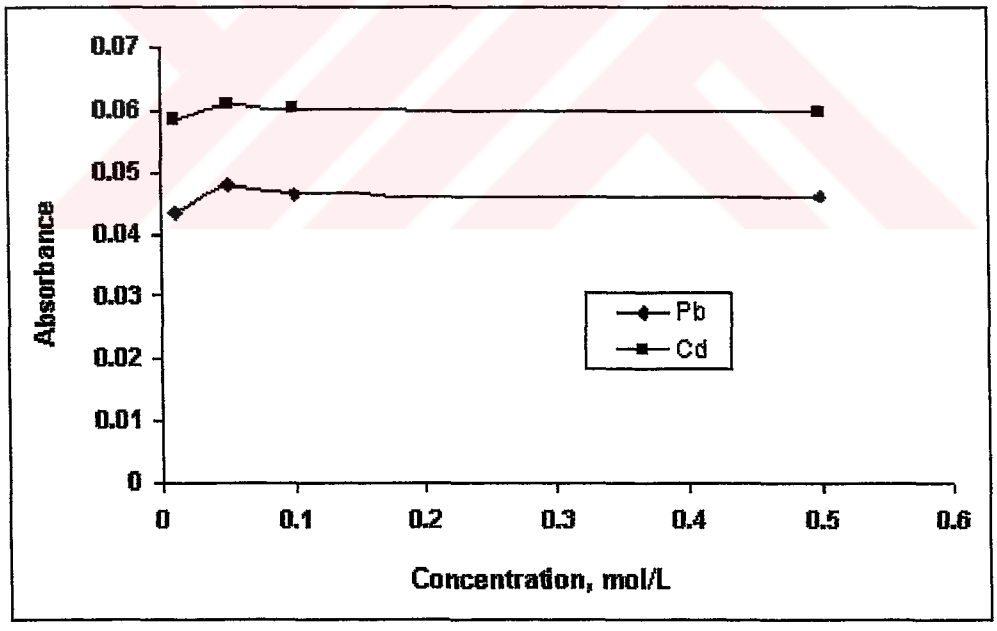

Figure 4.7. Effect of the concentration of the desorbing agent.

4.3.4. Effect of eluent flow rate

The influence of the eluent (0.1 mol L^{-1} HCl) flow rate on desorption of lead and cadmium ions from the minicolumn was investigated in the range of 3.4 mL min^{-1} to 5.7 mL min^{-1} after loading the column with 100 μg L^{-1} lead and 10 μg L^{-1} cadmium and (at 5.0 mL min^{-1} flow rate). As shown in Figure 4.8, the analytical signals obtained remained constant with increasing flow rates, probably due to the high desorption kinetics. Pb(II) and Cd(II) ions were released easily from the resin, presumably due to their ability to form Cl^- complexes. A flow rate of 5.0 mL min^{-1} was selected in the subsequent studies without forming air bubbles during aspiration.

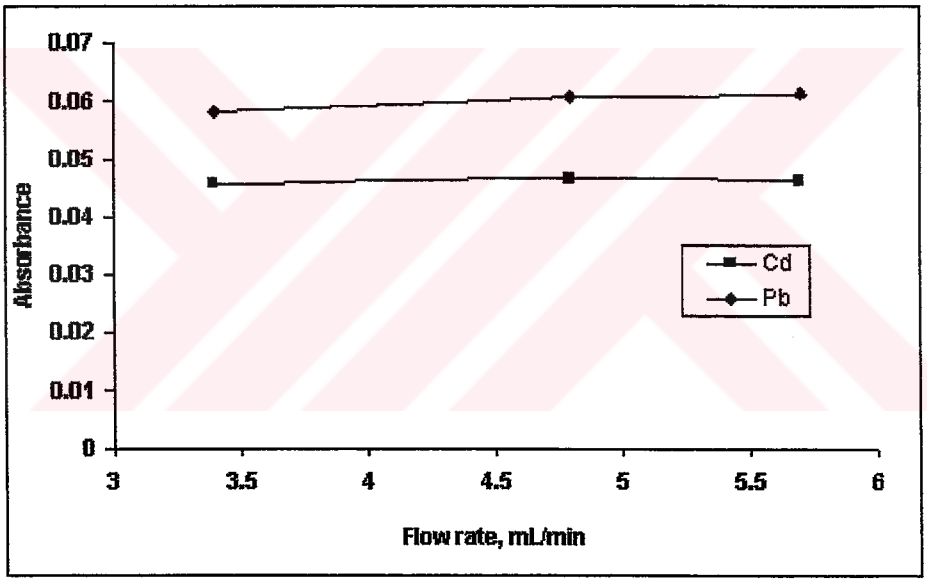

Figure 4.8. Effect of the flow rate of the desorbing agent.

4.3.5. Effect of electrolytes

The effect of KCl on the sorption of Pb(II) and Cd(II) ions was investigated. A set of solutions (volume of 100 mL each) containing varying amounts of electrolyte (ranging between 745 μg and 7450 μg) containing Pb(II) (10 μg) and Cd(II) (1 μg) were taken and the same adsorption and elution procedure was applied. The results are shown in Table 4. 3. KCl interferes in the adsorption of lead and cadmium ions above the ratio of 10 μg Pb(II)/7450μg KCl and 1 μg Cd(II)/4000 μg KCl, respectively. In table 4.3, all values are given as percentage variation in the atomic absorption signal (average of three replicate measurements).

Table 4.3. Effect of KCl on the sorption of Pb(II) and Cd(II) ions.

Metal ion	Ratio	Absorbance variation
	metal ion (μg)/KCl (μg)	(%)
Pb(II)	10/745	+9 ± 0.7
	10/2000	+7 ± 0.6
	10/4000	+3 ± 0.5
	10/7450	-9 ± 0.4
Cd(II)	1/745	+9 ± 0.6
	1/2000	+6 ± 0.6
	1/4000	-7 ± 0.7
	1/7450	interferes

4.3.6. Reusability of the pHEMA-thiazolidine microbeads

The reusability of the resin was tested by loading Cd(II) ions several times on a minicolumn from a solution (100 mL) having a concentration of 0.1 – 2 mg L^{-1} at a flow rate of 0.8 – 5.0 mL min^{-1} and eluting it by the recommended procedure. It was found that the adsorption capacity after 17 cycles of adsorption and desorption does not vary more than 2%. Therefore, multiple use of the resin is feasible. Similar results were also shown by the batch method.

4.3.7. Analytical features

By employing the optimum experimental conditions, i.e., chemical and flow conditions, the calibration graphs obtained for lead and cadmium respectively were:

$A = 0.0206[Pb, \mu g\ L^{-1}] + 0.0013$ $(R^2 = 0.9996)$

$A = 0.2302[Cd, \mu g\ L^{-1}] + 0.0073$ $(R^2 = 0.9999)$

in the interval of 0.0-25.0 $\mu g\ L^{-1}$ for lead and 0.0-10 $\mu g\ L^{-1}$ for cadmium. On the other hand, without the preconcentration procedure, i.e.,direct aspiration, the calibration graphs for lead and cadmium were:

$A = 0.0007[Pb, \mu g\ L^{-1}] - 0.0083$ $(R^2 = 0.9993)$

$A = 0.0109[Cd, \mu g\ L^{-1}] - 0.0066$ $(R^2 = 0.9991)$

By calculating the ratio of the slopes of the two equations above, i.e., with and without preconcentration, for each metal ions the preconcentration factors obtained were 29 and 21 for lead and cadmium, respectively.

The precision of the proposed preconcentration method was evaluated by using 25 $\mu g\ L^{-1}$ of Pb standard solution, yielding a R.S.D. of 8.3% (n=11); and by using 10 $\mu g\ L^{-1}$ of Cd standard solution, yielding a R.S.D. of 6.6% (n=11). The limits of detection, i.e., metal ion concentration having a response equivalent to three times the standard deviation (3σ) of a blank were found to be 11.2 $\mu g\ L^{-1}$ for Pb(II) and 5.6 $\mu g\ L^{-1}$ for Cd(II) based on eleven replicate determinations of the blank.

4.3.8. Accuracy of the method

In order to study the accuracy of the proposed method, the optimum experimental conditions were applied to tap water samples spiked with 15 μg L^{-1} and 30 μg L^{-1} lead, and 10 μg L^{-1} and 20 μg L^{-1} cadmium. The results obtained are summarized in Table 4.4.

Table 4.4. Obtained results for lead and cadmium in tap water samples.

Ion	Added, μg/L	Found, μg/L	Recovery,%
Pb(II)	15	14.54 ± 0.11	97
	30	29.44 ± 0.13	98
Cd(II)	10	11.02 ± 0.08	100
	20	22.16 ± 0.12	100

4.3.9. Competetive Adsorption of Pb(II) and Cd(II) Ions in Tap Water Sample

In this group of experiments, competitive adsorption of Cd(II) and Pb(II) ions from tap water samples containing the ions together was investigated. Optimum experimental conditions (sample solution and eluent flow rate, 5.0 mL min^{-1}; pH=5.3) were applied to tap water samples (volume of 100mL each) spiked with 30 μg L^{-1} Pb(II) and 10 μg L^{-1} Cd(II) ions, and 20 μg L^{-1} Pb(II) and 20 μg L^{-1} Cd(II) ions. When these results are compared with the values obtained in non-competitive on-line preconcentration from tap water solution experiments, it can be clearly seen that the presence of the ions together, adsorption amount of immobilized thiazolidine ligand for each metal ions after the on-line preconcentration procedure does not change. The results obtained are summarized in Table 4.5.

Table 4.5. Competitive adsorption in tap water samples.

Ion	Adsorption (μg/L)	
	Non-competitive	Competitive
Pb(II)	29.44 ± 0.11	30.83 ± 0.16
Cd(II)	11.02 ± 0.08	10.96 ± 0.11
Pb(II)	19.97 ± 0.33	21.31 ± 0.42
Cd(II)	21.23 ± 0.17	20.94 ± 0.24

When we compare the results obtained with on-line preconcentration system and batch procedure, it can be clearly seen that the immobilized thiazolidine ligand shows high affinity to Pb(II) ions in the batch procedure but do not in the on-line preconcentration system because of very low concentrations of metal ion solutions was used in on-line preconcentration system compared with an batch experimental set-up.

5. CONCLUSION

A novel metal complexing ligand thiazolidine carrying poly (hydroxyethylmethacrylate) microbeads for the removal of Cd(II) and Pb(II) ions from aqueous solutions were prepared. The adsorption and desorption properties of thiazolidine-immobilized pHEMA microbeads for Cd(II) and Pb(II) ions were investigated in batch and on-line continuous column systems.

pHEMA microbeads were prepared by a suspension polymerization technique and then thiazolidine was covalently immobilized onto the pHEMA microbeads. The nucleophilic substitution reaction was started by adding pHEMA microbeads.

The equilibrium swelling ratio of the pHEMA-thiazolidine microbeads used in this study was calculated as 58%. Compared with pHEMA (55%), the water uptake ratio of the pHEMA-thiazolidine microbeads was increased.

From the elemental analysis results, the amount of thiazolidine immobilized onto pHEMA microbeads was calculated as 0.318 mmol g^{-1} from the nitrogen and sulphur stoichiometry.

When the FTIR spectrum of pHEMA and thiazolidine immobilized pHEMA microbeads were compared it can be seen that the band at 1562 cm^{-1} is characteristic C-N stretching band (amide) due to thiazolidine bonded to pHEMA.

The effect of pH on adsorption of metal ions onto the thiazolidine immobilized pHEMA was investigated in batch processes . A rapid increase in binding of lead and cadmium occurred between pH 3.0 – 5.0 and 3.0 – 6.0 respectively and reaching plateau values at around pH 5.0 and 6.0 for Pb(II) and Cd(II) respectively.

Also, in batch experiments, adsorption rates of Pb(II) and Cd(II) ions by thiazolidine attached pHEMA as a function of time were investigated. High adsorption rates are observed at the beginning, and then plateau values (i.e.,adsorption equilibrium) are gradually reached within 10 min for both metal ions.

The adsorption capacities of the thiazolidine immobilized pHEMA microbeads were found as 0.336 mmol per gram of the sorbent (69.62 mg g^{-1}) for Pb(II) and 0.397 mmol g^{-1} of the sorbent (44.62 mg g^{-1}) for Cd(II).

When the competitive adsorption of Cd(II) and Pb(II) ions from solutions containing the ions together was investigated in the batch experiment the adsorption amounts were found as 0.0356 mmol g^{-1} for Cd(II) and 0.326 mmol g^{-1} for Pb(II). It is clearly seen that immobilized thiazolidine ligand shows high affinity to Pb(II) ions. Cd(II) affinity of thiazolidine is almost negligible according to Pb(II) ions.

Desorption of metal ions from the loaded samples was carried out by using 0.05 mol L^{-1} hydrochloric acid solution.

Resorption capacity of the sorbent for both metal ions did not change significantly during repeated adsorption-desorption operations.

The effect of column length and internal diameter on the preconcentration of lead and cadmium was examined and a minicolumn, 70 mm x 9 mm i.d., was chosen for analyte preconcentrations.

The maximum amounts of lead and cadmium adsorbed by thiazolidine immobilized pHEMA microbeads were found at pH 5.3 and pH 5.6, respectively. Therefore, pH 5.3 for lead and 5.6 for cadmium were selected for subsequent works after considering that , at lower values, complexation and retention incomplete, and at higher values (especially at pH 6) the performance of the chelating polymer decreasing rapidly.

Effect of the flow rate of the sample solutions was examined under the optimum conditions (pH, eluent, etc.) in a range varying from 0.8 mL min^{-1} to 5.7 mL min^{-1}. The results showed that the analytical signals obtained remained independent with increasing flow rates. These results were an indication of the fast adsorption kinetics for both of Pb(II) and Cd(II) adsorption.

The desorptions of lead and cadmium from the minicolumn were investigated by using various concentrations of HCl solution .It was observed that the elution was complete at 0.05 mol/L HCl concentration at the optimum conditions and 0.1 mol L^{-1} HCl solution was chosen as eluent. Also the influence of the 0.1 mol L^{-1} HCl solution flow rate in the step of lead and cadmium desorption from the minicolumn was investigated between the range of 0.8 mL min^{-1} and 5.7 mL min^{-1}. The analytical signals obtained remained constant with increasing flow rates, probably due to the high desorption kinetics. Pb(II) and Cd(II) ions were released easily from the resin, presumably due to their ability to form Cl^- complexes. A flow rate of 4.8 mL min^{-1} was selected in the subsequent studies without forming air bubbles during aspiration.

The reusability of the resin was tasted. It was found that the adsorption capacity after 17 cycles of adsorption and desorption does not vary more than 2%. Therefore, multiple use of the resin is feasible.

By calculating the ratio of the slopes of the two absorbance equations obtained with and without preconcentration, for each metal ions the preconcentration factors obtained were 29 and 21 for lead and cadmium, respectively.

The precision of the proposed preconcentration method was evaluated by using 25 $\mu g\ L^{-1}$ of Pb standard solution, yielding a R.S.D. of 8.3% (n=11); and by using 10 $\mu g\ L^{-1}$ of Cd standard solution, yielding a R.S.D. of 6.6% (n=11). The limits of detection, i.e., metal ion concentration having a response equivalent to three times the standard deviation (3σ) of a blank

were found to be 11.2 μg L^{-1} for Pb(II) and 5.6 μg L^{-1} for Cd(II) based on eleven replicate determinations of the blank.

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