Functionalizion Of Alumina With Methionine As Solid Phase For Selective Ion Exchange And Preconcentration Of Heavy Metals

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ABSTRACT

Methionine as an example of amino acids and environment friendly compound was used to modify the surface of alumina via physical adsorption approach in a clean and green chemical procedure. Three newly synthesized alumina phases, acidic(I), neutral (II) and basic(III) were prepared and charecterization of surface modification was accomplished by study the mass spectrometric analysis and infrared as well as determination of surface coverage by thermal desorption and metal probe testing methods. The metal sorption properties of modified alumina-physically adsorbed-methionine phases(I-III) were also studied and evaluated for a series of metal ions under various buffer solutions and shaking times as controlling factors. Methionine-modified-alumina as new solid phase extractors were experienced with good incorporated selectivity characters toward Pb(II), Cr(III) and Fe(III) based on determination and evaluation of the distribution and separation factor values. The utilization and application of modified alumina phases(I-III) for selective extraction and preconcentration of ppm and ppb concentration levels of these metal ions from real drinking and waste water samples were successfully accomplished with excellent recovery values and without interference of the matrix.
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INTRODUCTION

Inorganic solid supports such as alumina is commonly used in different fields and applications of analytical chemistry. Various alumina types are widely known for their differences in chemical and physical properties[1]. The surface of alumina is characterized by the presence of hydroxyl groups with various arrangements and distribution as the major contributors in binding, adsorption, and extraction processes. The weak ion exchange properties of hydroxyl groups are to favor their low interaction behavior with various species[2]. Therefore, improvements of the adsorption efficiency and extraction power of these alumina phases via incorporation of certain functional groups are always aimed by surface modification. Different techniques are usually applied to modify alumina surface including surfactant coating followed by direct immobilization of the modifier of interest either organic or inorganic for synthesis and formation of modified alumina phases[3]. Chemical modification of alumina surface, also denoted as chemisorption, can be accomplished by two distinct processes: organofunctionalization, where the modifier reagent is organic compound and inorganofunctionalization, in which the group anchored on the surface may be an organometallic or a metallic oxide[4]. Surface modification of alumina phases can also be performed by sol-gel technique in which a polymer coating procedure of the surface and precipitation of the modifier[5]. Modification of alumina phases with organic or inorganic modifiers can also be accomplished by physical adsorption approach via thermal or hydrothermal treatment. This approach is very simple compared to other methods and considered as time, efforts and money saver as well as being friendly to the environments. This technique of surface modification leads to chemical change in the surface composition of modified alumina phases. The most convenient way to develop physisorbed alumina phases is usually achieved by simple immobilization of the target compound on the alumina surface via adsorption, electrostatic interaction or hydrogen bond formation[6].

Metal ions and their species either essential or toxic for the living organisms are finding their routes into the different samples, matrices and environments from many sources. The accurate determination, qualitative or quantitative analysis, of the target metal ions or their species especially in the environmental, biological and industrial samples are considered of great challenge to analytical chemists because of the huge number of interfering species and compounds. The determination procedure is principally started with an important step known as the extraction and/or preconcentration. Several available techniques are commonly used and applied in metal ions extraction[7,8]. The solid phase extraction technique (SPE) affords several advantages over the classical liquid extraction concerning the hazardous waste generation. SPE is mainly based on the utilization of solid support, either organic or inorganic, instead of organic solvent to load the target metal ion or analyte on the surface. Functionalized chelating inorganic solid supports are the most important types of sorbents that can be used and applied in solid phase extraction of toxic and non-toxic metal ions due to incorporated selectivity characters via the presence of certain donor atoms, mainly nitrogen, oxygen, sulfur and phosphorus in these modified SPE.

Methionine is characterized by the presence of three donor atoms or groups namely, oxygen, nitrogen and sulfur atoms, based on the presence of carboxylic, amino and thioether functional groups. These donor atoms were found to incorporate some physical and chemical characters into methionine. The chelating characters incorporated into methionine were found to be highly appreciated as an important spectrophotometric reagent for the determination of various metal ions[9,10]. In addition, utilization of methionine in chromatographic and separation applications are also evident[11-13]. Applications of methionine based on other separation techniques were also reported[14-16].

Immobilization of methionine as a chelating compound on the surface of alumina phases for the sake of use in metal selective extraction and preconcentration applications was not previously reported. Therefore, we aimed to study the possible binding or loading of methionine via physical adsorption approach on the surface of three alumina phases, namely acidic, neutral and basic, for further investi-

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gation in the field of normal or selective metal exraction, removal, separation and preconcentration from different samples and matrices.

EXPERIMENTAL

Instrumentation

Thermolyne 47900 furnace was used to determine the mmol g^{-1} surface coverage values of modified alumina phases via thermal desorption analysis. Infrared spectra of alumina phases(I-III) were recorded from KBr pellets using a Perkin-Elmer spectrophotometer, model 1430. The pH-measurements of the metal ions and buffer solutions were carried out with an Orion 420 pH-meter and this was calibrated against standard buffer solutions of pH 4.0 and 9.2. Atomic absorption analysis for determination of the metal concentration was performed using a Shimadzu model AA-6650. The electron impact mass spectra of blank alumina, methionine and modified alumina phases(I-III) were carried out using a Varian MAT 212 mass spectrometer equipped with a direct insertion probe(DIP) in the Institute for Inorganic and Analytical Chemistry, Muenster University, Germany.

Solutions

The metal ion solutions were prepared from doubly distilled water(DDW). Buffer solutions(pH 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0) were prepared from 1.0 M-hydrochloric acid solution and 1.0 M-sodium acetate trihydrate solution by mixing the appropriate volumes of the two solutions and diluting to 1.0 liter. The pH-values of resulting solutions were adjusted by a pH meter. The metal salts are all of analytical grade and purchased from Aldrich Chemical Company, USA and BDH Limited, Poole, England.

Chemicals and reagents

Methionine and three alumina types of standard specifications(150 mesh, 58 A^0, and surface area=155 m^2/g) were purchased from Aldrich Chemical Company, USA and used as received. The first alumina type is an acidic with a pH value of 4.5±0.5 of the aqueous suspension. The second alumina type is neutral with an assigned pH 7.0±0.5 of aqueous sus-

pension and the third alumina phase is a basic type with a pH value of 9.5±0.5.

Synthesis of alumina phases-physically adsorbed-methionine(I-III)

1.5 g (~10.1mmol) of methionine(Formula weight=149.21 and melting point=280^{0}C) was weighed and transferred to a 250ml conical flask. A mixture of 100ml of distilled water and 60ml of ethyl alcohol was then added to this sample and allowed to stir on cold until complete dissolution of the organic modifier, methionine. To this solution 10.0± 0.1g of alumina phase, either acidic, neutral or basic, was added and the reaction mixture was further stirred for six hours. The newly modified alumina phases were filtered, washed with water and ethyl alcohol and allowed to dry in an oven at 60^{0}C.

Surface coverage determination and stability test of alumina phases(I-III) in acidic buffer solutions

Thermal desorption method[17,18] was used to determine the surface coverage values of modified alumina phases (I-III). In this method, 100±1mg of dry alumina phases(I-III) was weighed and ignited at 550^{0}C in a muffle furnace. The initial temperature was set at 50^{0}C and gradually increased to 550°C in about 20 minutes. The ignited phase was then kept at this temperature for one hour and left to cool down inside the furnace till 70^{0}C. The weight loss of organic chelating compounds was determined by difference in the sample weights before and after the process of thermal desorption. Blank samples of alumina phases were also subjected to the same thermal desorption procedure as described for comparison with the results obtained for alumina phases-physically loaded-methionine.

To perform the stability test, the modified alumina phase(0.5g) was mixed with 50 ml of the selected buffer solutions(pH 1-7) in a 100ml volumetric flask and automatically shaken for one hour. The mixture was filtered, washed with another 50ml portion of the same buffer solution and DDW and dried at 70^{0}C. The buffered alumina phase(25.0±1 mg) was added to a solution containing 9.0ml of buffer solution(pH=6) and 1.0ml of 0.1 molar of Cu(II). The mixture was automatically shaken for 30 min-

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utes and the degree of hydrolysis of alumina phase-physically adsorbed-methionine in different buffer solutions was determined from the metal uptake values of Cu(II).

Determination of metal capacity

This series of metal ions, Mg(II), Ca(II), Mn(II), Cr(III), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and Pb(II) were selected to determine the metal capacity values(μmol g^{-1}) of the modified alumina phases(I-III) in various buffer solutions (pH 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0). 50±1 mg of the dry phase was weighed, added to a mixture of 1.0 ml of 0.1M metal ion and 9.0ml of the selected buffer solution into a 50ml measuring flask. These were shaken at room temperature for 30 minutes by an automatic shaker. After equilibration, the mixture was filtered and washed three times with 100ml-DDW. The unbounded metal ion was subjected to complexometric titration using 0.01M-EDTA solution or by atomic absorption analysis.

The effect of shaking time intervals(1,5,10,15, 20,25 and 30 minutes) on the metal capacity and the percentage of extraction was also studied for some selected metal ion by the batch equilibrium technique according to the following procedure. The dry alumina phase(50±1mg) was added to a mixture of 1.0 ml of 0.1M of each metal ion and 9.0ml of the optimum buffer solution. This mixture was shaken for the selected period of time, filtered, washed with 100 ml DDW and the unextarcted metal ion by alumina phase was determined by complexometric EDTA titration.

Determination of the distribution coefficient

The tested metal ions are Mg(II), Ca(II), Mn(II), Cr(III), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II). The concentration of each metal ion solution is ~1.0ppm in 0.1 molar sodium acetate solution except Fe(III) was prepared in buffer pH 2. In a 25ml measuring flask, 100±1mg of the modified alumina phase (I-III) was weighed. 10ml of 1.0 ppm metal ion was then added and the flask was shaken by an automatic shaker for 1-hour. This mixture was filtered and washed with 10 ml DDW. The volume of metal ion was completed to 50ml by using 5% nitric acid solution. Standard and blank solutions of

the same metal ion were also prepared. The concentration of metal ion in the sample, standard and blank solutions were determined by atomic absorption analysis.

Applications of modified alumina phases(I-III) for selective removal and extraction of Pb(II) from industrial waste water samples

Waste water samples were collected from Damnhour drug factory and spiked with ~1.0-2.0 ppm Pb(II) followed by flame atomic absorption analysis of these samples. The extraction procedure of Pb(II) from water sample was accomplished by running 1.0 liter over a micro-column packed with 500 mg of the selected modified alumina phase with a flow rate 10.0ml min^{-1}. The effluent solution was collected and acidified with nitric acid and subjected for atomic absorption spectrophotometric analysis of the free unextarcted metal ion. The water sample was subjected for atomic absorption spectrophotometric analysis before running over the tested column. A blank sample was also measured by atomic absorption spectrophotometric analysis for the direct comparison.

Selective preconcentration of Pb(II) from drinking tap water samples

Preconcentration of Pb(II) was performed according to this procedure. 1.0 liter of drinking tap water sample was spiked with(~1.0 and 5.0 ng ml^{-1}) of the target metal ion. This water sample was passed over a preconcentration micro-column packed with 100mg-modified alumina phase(I-III) with a flow rate of (~10.0ml min^{-1}). The adsorbed metal ion on the alumina surface was desorbed by the flow of 5.0ml of concentrated nitric acid and determined by atomic absorption analysis to identify the percentage recovery and preconcentration values.

RESULTS AND DISCUSSION

Characterization of surface modification

1. Electron impact mass spectrometry of modified alumina phases (I-III)

Mass spectrometry technique is one of the powerful analytical methods for qualitative and quanti-

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tative determination of organic and inorganic compounds[19]. Several techniques are usually used to apply the sample into the mass spectrometer and the ionization chamber. The most commonly used sample application methods are the direct insertion probe (DIP). In this, the sample is loaded on a probe tip and heated to allow sample evaporation and insertion into the ion source. The probe temperature of 200-300^{0}C is usually applied and sufficient for evaporation of the sample molecules and detection by the mass spectrometric detector. Thus, the mass spectrometric technique can be used to study the volatilization of the organic compounds by the direct insertion probe. Alumina phases-chemically or physically loaded-organic compounds can be tested for surface modification as well as thermal stability via their analysis by the mass spectrometric technique under electron impact ionization with a heating range reaching 300-350^{0}C in a way similar to that described and known for pyrolysis of polymer compounds by mass spectrometric technique[20].

The 70-eV electron impact-mass spectra(70-eV EI-MS) as determined by the direct insertion probe (DIP) and heated to 300-350^{0}C as a maximum heating temperature of methionine and blank alumina phases were studied for comparison with modified alumina phases(I-III). The mass spectrum of blank acidic alumina is characterized by the presence of two characteristic low masses at m/z 18 and 44 as the major peaks. The peak at m/z 18 is mainly due the presence of either adsorbed water molecules on the surface of blank alumina phase or presence of water molecules inside the ionization chamber of the mass spectrometer. The latter attribution is assisted by the presence of a mass peak at m/z 44 which corresponds to the presence of CO_2 molecule[21]. No other characteristic fragment ion peaks can be identified from the mass spectrum of blank alumina phase. The 70-eV EI-MS-DIP spectrum of methionine is characterized by the molecular ion at m/z 149(100%) as the base. In addition, two other fragment ions at m/z 132(14%) and 131(78%) and these are related to the loss of hydroxyl group or water molecule from the molecular ion, respectively. Some other fragment ion peaks are derived and related to the methionine moiety at 104(32%) for loss

of the carboxyl group, 102(42%) for the loss of [CH_3S] from the molecular ion, 75(53%) for the formation of this fragment ion [CH_3SCHNH], 61(98%) for this fragment ion [CH_3SCH_2] and 47(12%) for the formation of this fragment ion [CH_3S]. The 70-eV EI-MS-DIP spectrum of acidic alumina-physically adsorbed-methionine(I) was found to give masses at 18, 28 and 44 known to be related to H_2O, N_2 and CO_2 molecules, respectively. The other fragment ions are of very low relative abundance and this trend is expected owing to the low percentage value of immobilized methionine on the surface of acidic alumina(4.4%) which is calculated from the surface coverage of phase(I). Very low abundant molecular ion peak at m/z 149(2%) as well as only an identified fragment ion at m/z 47 for the formation of fragment ion [CH_3S].

The same trends and observation can be identified and outlined from the 70-eV EI-MS-DIP spectra of modified neutral alumina phase(II) and modified basic alumina phase(III). The percentage surface coverage values are calculated from the corresponding surface coverage values and found 4.2 and 4.9%, respectively. The conclusion that can be drown from the mass spectrometric study of these phases at the measured temperature of DIP(300-350^{0}C) is the capability of 70-eV EI-MS-DIP technique for study confirmation of surface adsorption of methionine on either acidic, neutral or basic alumina phase. The thermal stability of these newly modified alumina phases can also be confirmed due to the absence of good mass fragment patterns in these phases as compared to the 70-eV EI-MS-DIP of methionine.

2. Evaluation of surface characterization by infrared

The infrared of blank alumina phases are identified by the presence of three peaks at 3600-3400, 1650 and 1000-400cm^{-1} that are mainly due to alumina matrix. These predominating characteristic peaks in newly synthesized alumina phases(I-III) were also exhibited irrespective of the loaded organic modifier. This may be attributed to the overlapping of the majors functional groups of methionine as OH, CO and CSC by the frequency of these three predominating peaks. In addition, the low surface coverage of alumina phases with methionine is con-

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sidered as the basic reason for such overlap of very weak bands of the organic modifier as well as intra- and inter-molecular hydrogen bonding with these three characteristic peaks of alumina.

3. Determination of surface coverage

The determination of the surface coverage values of modified phases can be accomplished by several well known methods such as the thermal desorption method and the metal probe testing method[17,18,22]. The determined surface coverage values on the basis of thermal desorption method were found 0.298, 0.284 and 0.330mmol g^{-1} for newly modified alumina-physically adsorbed-methionine(I), (II) and (III), respectively. The closeness in the surface coverage mmol g^{-1} values for these modified alumina phases(I-III) proves that there is no role for the acid-base characters of the blank unmodified acidic, neutral and basic alumina phases in the process of the physical adsorption. The second method used in this work for determination of the surface coverage values is the metal probe testing[22]. According to this method the estimated surface coverage mmol g^{-1} values for modified alumina phases-physically adsorbed-methionine (I), (II) and (III) were found to correspond to 0.360, 0.380 and 0.380mmol g^{-1}, respectively based on the values of metal capacity of Cu(II). The reason for such high surface coverage determination by this method may be attributed to the contribution of the alumina matrix via ion exchange characters incorporated into these types of solid supports[23]. TABLE 1 compiles the calculated and evaluated surface coverage values of the three newly modified alumina phases-physically adsorbed-methionine(I-III) as determined by the thermal desorption and

TABLE 1: The surface coverage values of alumina phases-physically adsorbed-methionine(I-III)

Alumina phase	pH-value	Thermal desorption mmol g^{-1}	Metal probe mmol g^{-1}
Blank acidic alumina	4.4	-	-
Blank neutal alumina	6.7	-	-
Blank basic alumina	8.9	-	-
Modified acidic alumina	4.2	0.298	0.360
Modified neutal alumina(I)	5.3	0.284	0.380
Modified basic alumina	5.8	0.330	0.380

metal probe testing methods. The pH-values of the blank alumina and modified alumina phases(I-III) are also listed.

4. Stability of the newly modified alumina phases in different acidic pH solutions[24]

The stability of newly modified alumina phases-physically adsorbed-methionine(I-III) in different acidic buffer solutions(pH 1-7) was tested to identify the possible degree of leaching or hydrolysis of the organic chelating modifier, methionine, from the surface of each alumina phase. The hydrolyzed alumina phase was then used to determine the mmol g^{-1} of Cu(II). The values of determined mmol g^{-1} for the hydrolyzed alumina phase was compared with the unhydrolyzed alumina phase to calculate the percentage values of stability for each alumina phase in the tested buffer solutions. TABLE 2 compiles the results obtained for stability towards hydrolysis and leaching process of modified alumina phases-physically adsorbed-methionine(I-III). It is evident from

TABLE 2: Stability of modified alumina phases(I-III)*

pH	Alumina phase(I)		Alumina phase(II)		Alumina phase(III)	
	% Stability	(μmol g^{-1})	% Stability	(μmol g^{-1})	% Stability	(μmol g^{-1})
1.0	61.1%	(0.22)	52.6%	(0.20)	57.9%	(0.22)
2.0	55.5%	(0.20)	52.6%	(0.20)	57.9%	(0.22)
3.0	83.3%	(0.30)	57.9%	(0.22)	63.2%	(0.24)
4.0	61.1%	(0.22)	57.9%	(0.22)	57.9%	(0.22)
5.0	61.1%	(0.22)	57.9%	(0.22)	57.9%	(0.22)
6.0	61.1%	(0.22)	57.9%	(0.22)	52.6%	(0.20)
7.0	66.7%	(0.24)	57.9%	(0.22)	52.6%	(0.20)

*Values are based on triplicate analysis

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the data given that acidic alumina phase(I) is highly stable in buffer solution with pH 3 giving a percentage stability value of 83.3%, while in most of the other tested buffer solutions the percentage stability values were in the range of 55.5-61.1%. On the other hand, neutral alumina phase-physically adsorbed-methionine(II) was found to give almost the same percentage stability value of 57.9% in the buffer solutions of pH 3.0-7.0. Basic alumina phase-physically adsorbed-methionine(III) was found to give the highest percentage stability value in buffer solution pH 3.0 and the other percentage values are ranging in 52.6-57.9%.

Metal binding properties of modified alumina phases(I-III)

Determination of the metal capacity values in either mmol g^{-1} or μmol g^{-1} or any other form is considered as an essential procedure for evaluation of the capability of newly modified alumina phases(I-III) to bind and use in solid phase extraction of different metal ions from aqueous solutions. Two major factors are important in the evaluation processes used for determination of the metal capacity values[25]. (i) The effect of pH of contact solution that contain both metal ion and alumina phase. (ii) The effect of shaking time when the batch equilibrium technique is used or the effect of flow rate when the column technique is applied.

1. Effect of pH-value on the metal capacity

The effect of pH of tested metal ion solutions on the amount extracted by the modified alumina phase is considered as the major important factor in such procedure because of the liability of most metal ions to be strongly influenced by free or immobilized chelating compound as methionine at certain pH values. TABLE 3 summarize the determined metal capacity values for binding various metal ions, expressed in μmol g^{-1}, in the buffer solutions with pH 5, 6 and 7. It is evident from the data given in TABLE 3 of the newly modified alumina phase(I) that Cr(III) is the highest extracted metal ion in buffer solutions pH 5.0 and 6.0 with a metal capacity of 170 and 130μmol g^{-1}, respectively while the maximum metal capacity value of Cr(III) and Cu(II) were found to be 360μmol g^{-1} as the highest extracted and bound to modified alumina phase in buffer solution of pH 7.0. However, Fe(III) was only examined in buffer solutions with pH 1.0-4.0 to avoid any precipitation of Fe(OH)$_3$ at buffer solutions with pH 5-7. The maximum metal capacity values for Fe(III) were found 150μmol g^{-1} in buffer solutions.

TABLE 3 compiles the metal capacity values determined by the newly modified neutral alumina phase(II). It is evident that Cr(III) is the highest extracted metal ion in buffer solutions pH=5.0 and 7.0 with a metal capacities of 180, 390μmol g^{-1} respectively. The determined metal capacity values for

TABLE 3: Metal capacity(μmol g^{-1}) of alumina phase (I),(II) and (III) in buffer solutions (pH 4-7)*

Metal ion	Phase(I)			Phase(II)			Phase(III)		
	pH 5.0	pH 6.0	pH 7.0	pH 5.0	pH 6.0	pH 7.0	pH 5.0	pH 6.0	pH 7.0
Mg(II)	00	00	00	00	00	00	00	00	00
Ca(II)	00	00	00	00	00	00	00	00	00
Cr(II)	170	130	360	180	140	390	190	150	390
Mn(II)	00	00	10	00	00	20	00	00	10
Fe(II)	60	120	150	60	170	190	70	170	220
Co(II)	00	00	00	00	00	00	00	00	00
Ni(II)	00	00	00	00	00	00	00	00	00
Cu(II)	30	100	360	40	120	380	40	130	380
Zn(II)	00	40	100	00	50	110	00	50	120
Cd(II)	00	00	10	00	00	10	00	00	10
Hg(II)	00	00	00	00	00	00	00	00	20
pb(II)	20	50	160	20	60	210	30	60	230

*Values are based on triplicate analysis.
** Metal capacity values of Fe(III) in pH 2, 3 and 4.

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Pb(II) by the newly modified neutral alumina phase-physically adsorbed-methionine(II) were found 20, 60 and 210μmol g^{-1} in buffer solution of 5.0, 6.0 and 7.0, respectively. These values along with other metal capacity values, as the case of Fe(III), Cu(II) and Zn(II), give evidences and refer to the contribution and effect of pH value of contact solution of metal and alumina phase on the determined values of metal capacity. In the same way, the calculated metal capacity values for Fe(III) were found to be 60, 170 and 190μmol g^{-1} in buffer solutions with pH values of 2, 3 and 4, respectively. TABLE 3 compiles the metal capacity values in μmol g^{-1} for the same series of metal ions in various buffer solutions(pH 4.0-7.0) except the values of Fe(III) were determined in buffer solution 2.0, 3.0 and 4.0. It is easy to figure out that newly modified alumina phase(III) is similarly behaving as modified alumina phases (I) and (II) toward binding and extraction of the tested metal ions especially, Cr(III), Fe(III) Cu(II) and Pb(II). The conclusions that can be drawn from this study can be outlined as follows:

(i) Some metal ions as Mg(II), Ca(II), Mn(II) Co(II), Ni(II) and Cd(II) were not highly extracted by the newly modified alumina phases(I-III) and were also not affected by the change of pH values of the contact solution.

(ii) The physical adsorption of methionine on the surface of either acidic, neutral or basic alumina phase type has little contribution to increase the selectivity of these phases(I-III) to the above mentioned metal ions.

(iii) The highest extracted metal ions by the newly modified alumina phases are Cr(III), Fe(III), Cu(II) and Pb(II).

(iv) The effect of pH values of the contact solution on the determined metal capacity values is clear for these four metal ions.

2. Effect of shaking time on the metal capacity

The effect of shaking time is the second most important factor when the batch or static technique is used in the processes of determination of metal capacity values by the newly modified alumina phases-physically adsorbed-methionine(I-III). The importance of the shaking time comes from the need for knowing the possible rapidness of binding and extraction of the tested metal ions by the newly modified phases. In addition, certifying the optimum time for complete extraction of the target metal ion is usually aimed for many reasons as the comparison with other well known modified phases or chelating polymers and it is usually useful when separation of metal ions from each other is aimed. For these reasons, Cu(II) and Pb(II) were selected for this study. Figure 1 represents the effect of selected shaking time values(1,5,10,15,20,25 and 30 minutes) on the percentage extraction of Pb(II) and Cu(II) by alumina phase (II) as an example. It was also concluded from this study that Pb(II) was similarly behaving toward extraction by the three newly modified alumina phases(I-III). Very close percentage extraction values can be outlined under the identical shaking time by the alumina phases(I-III). In other words, Pb(II) was found to show percentage extraction values of ~80% when only 5-minutes shaking time was used. This time shows also that fast equilibration of Cu(II) with alumina phases. In addition, there is no evidence of superiority of any phase in the extraction process of Cu(II), but only similar trends and behaviors. The only basic difference between the extraction of Pb(II) versus Cu(II) is the somewhat slowness of Cu(II) extraction by the three newly modified alumina phases(I-III). Between 15-20 minutes of shaking time were needed to reach a range of 80 % extraction of Cu(II) by alumina phases(I-III). However, complete extraction of Cu(II) by alumina phases (I-III) were reached at time >20-minutes of shaking time.

Determination of the distribution coefficient

Evaluation of the metal binding properties is considered more convenient by the distribution coefficient (K_d)[26] when the concentrations of the tested metal ions are very low especially in the range of part per million(ppm) or part per billion(ppb). The K_d-value is determined from the following equation:

$$K_d = \frac{\text{mmol of extracted metal ion / g - alumina phase}}{\text{mmol of unextracted metal ion / volume of solution}}$$

The distribution coefficient values for the modified alumina phase-physically adsorbed-methionine (I-III) are compiled in TABLE 6. It is evident that surface modification of different types of alumina
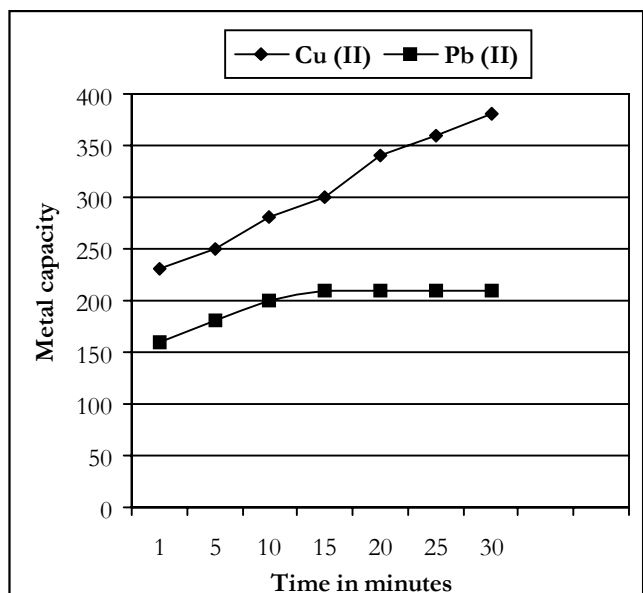
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Figure 1: Effect of shaking time on the metal capacity of Cu(II) and Pb(II) by modified alumina phases(II)

TABLE 6: The distribution coefficients values for the various metal ions by modified alumina phases (I-III)*

Metal ion	Phase(I)	Phase(II)	Phase(III)
Mg(II)	7	90	86
Ca(II)	10	40	517
Cr(II)	74	3394	17
Mn(II)	41	746	1097
Fe(II)	2825	2286	5884
Co(II)	37	1406	1452
Ni(II)	27	2330	1207
Cu(II)	91	1047	1381
Zn(II)	15	1714	6031
Cd(II)	10	3285	3004
Pb(II)	2889	72946	29829

*Values are based on triplicate analysis.

with methionine as an organic chelating modifier has led to change the chemical properties of alumina surface toward binding and extraction with certain metal ions. It is also clear from the data given in TABLE 6 that Pb(II) and Fe(III) are highly extracted by modified acidic alumina phase(I) based on their K_d values 2889 and 2825, respectively. The other tested metal ions were found to exhibit low distribution values by the unmodified acidic alumina(I) and these include Mg(II), Ca(II), Cd (II), Zn(II), Ni(II), Co(II), Mn(II), Cr(III) and Cu(II) . This conclusion can be confirmed by evaluation of the separation factors for these tested metal ions.

The distribution coefficient values for modified neutral alumina phase(II) confirm that Pb(II) is the highest extracted metal ion by modified neutral alumina phase(II) based on the K_d value 72946. The other tested metal ions were found to exhibit low distribution values by the modified neutral alumina (II). It is also evident that Pb(II), Zn(II) and Fe(III) are the highest extracted metal ions by modified basic alumina phase(III) based on their K_d values: 29829, 6031 and 5884, respectively as listed in TABLE 6. The other tested metal ions were found to exhibit low distribution values by the modified basic alumina(III) and these include, Mg(II), Ca(II), Mn(II), Cr(III), Ni(II), Cu(II), Co(II) and Cd(II). Thus

the order for increasing the distribution coefficient values for the tested metal ions by alumina phases(I-III) can be outlined in the following order:

K_d(Phase I): Mg(II) < Ca(II) <Cd(II) <Zn(II) <Ni(II) <Co(II) <Mn(II) <Cr(III) <Cu(II) <Fe(III) <Pb(II).

K_d(Phase II): Mg (II) < Ca(II) <Mn(II) < Cu(II) <Co(II) < Zn(II) < Fe(III) < Ni(II)< Cd(II) < Cr(III) < Pb(II).

K_d(Phase III): Cr(III)< Mg(II) < Ca(II) <Mn(II) <Ni(II) <Cu(II) <Co(II) <Cd (II) <Fe(III) < <Zn <Pb.

Separation factors of selected metal ions by alumina phases (I-III)

The separation factor[27,28] is one of the key points in the evaluation process of selective solid phase extraction of target metal ions from other interfering ions. The separation factor($\alpha_{A/B}$) of any two cations A and B is based on the distribution coefficient values K_d(A) and K_d(B), respectively as given in the following equation:

$$\alpha_{A/B} = \frac{K_d(A)}{K_d(B)}$$

The separation factor of Pb(II) versus other metal ions as well as Fe(III) versus other tested metal ions by modified acidic alumina phase(I) are shown and represented in figure 2. It is clear that Pb(II) can be selectively extracted from other interfering metal ions as Mg(II), Mn(II), Zn(II), Ca(II), Ni(II), Cr(III) and Co(II). Possible interference of some metal ions as Fe(III) and Cu(II), due to low separation factors of Pb(II) versus these metal ions. Figure 3 represents the separation factor of Pb(II) versus other tested metal
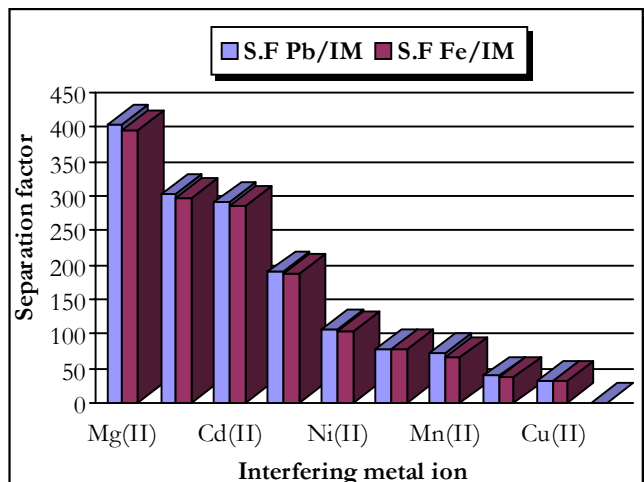
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Figure 2: Separation factors of Pb(II)&Fe(III) versus other interfering metal ions (IM) by phase(I)
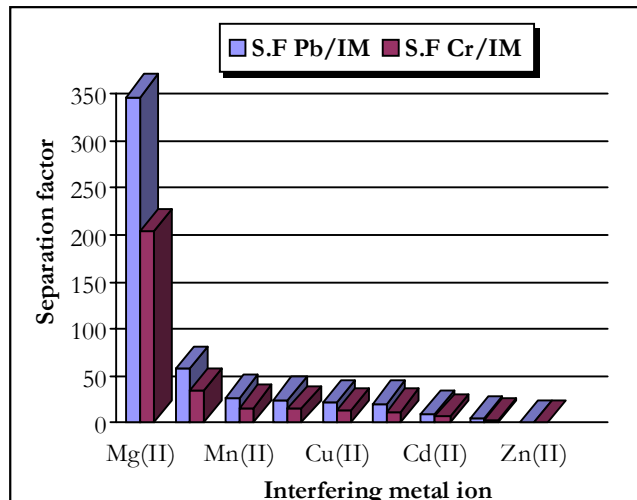

Figur 4: Separation factors of Pb(II) and Cr(III) versus other interfering metal ions(IM) by phase(III)
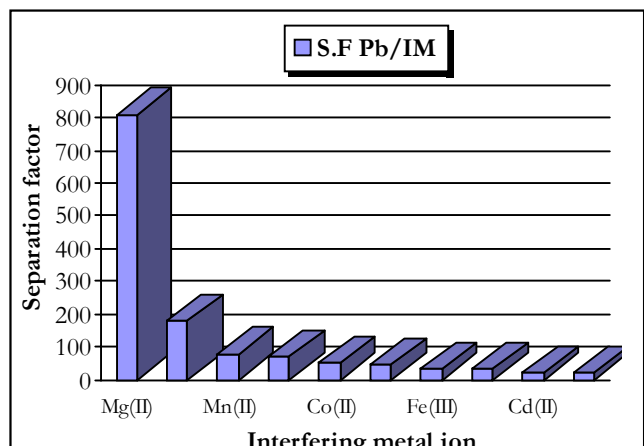

Figure 3. Separation factors of Pb(II) versus other interfering metal ions (IM) by phase(II)

ions by modified neutral alumina phase(II). Possible interference of only Cr(III) and Cd(II) are expected due to low calculated separation factors of Pb(II) versus these two metal ions. The separation factor of Pb(II) and Cr(III) versus other tested metal ions by modified basic alumina phase(I) are shown and represented in figure 4. It is clear that Pb(II) and Cr(III) can be selectively extracted from other interfering metal ions with possible interference of some metal ions as Fe(III), Zn(II) and Cd(II).

Selective solid phase extraction and removal of heavy metal from waste water by modified alumina phases (I-III)

Selective solid phase extraction and preconcentration of heavy metal ions from real samples is an-

other dimension for application of newly modified alumina phases[29]. The preconcentration technique, also known as enrichment, is a generic term for the various processes employed to increase the ratio of analyte of interest to the matrix. In the preconcentration procedures, the ratio of trace amount of desired analyte to that of the original matrix is usually converted into a new matrix suitable for analytical determination and evaluation. Preconcentration of trace concentration levels of heavy metal ions is an essential step for the sake of increasing the concentration of target metal ions in order to improve the sensitivity of instrumentation used as atomic absorption(AA) to meet and match with the linear dynamic range assigned for each metal ion by the atomic absorption. In addition, preconcentration increases the sensitivity by several orders of magnitude, enhances the accuracy of the results, offers high degree of selectivity and facilitates calibration[30].

This part is mainly based and dependent on the selectivity characters incorporated into alumina phases via physical adsorption of organic chelating modifier as methionine. TABLE 7 summarizes the results of selective metal extraction and removal of heavy metal ions as Pb(II), Fe(III) and Cr(III) from waste water samples collected from Damnhour drug factory. It evident from the percentage extraction values given in TABLE 7 that extraction of Fe(III) and Pb(II) by the newly modified alumina phase(I) is excellent judging from the 95.0 and 96.0% values.

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TABLE 7: Selective solid phase extraction and removal of heavy metal ions from waste water samples*

Alumina phase	Sample volume	Metal ion	$\mu g\ ml^{-1}$ Spiked	$\mu g\ L^{-1}$ Detected	Percent extraction
500-mg(I)	1.0 L	Fe(III)	1.172	0.051	$95.0 \pm 2\%$
		Pb(II)	2.021	0.065	$96.0 \pm 3\%$
500-mg(II)	1.0 L	Pb(II)	2.021	0.060	$97.0 \pm 3\%$
500-mg(III)	1.0 L	Cr(III)	0.972	0.027	$97.0 \pm 4\%$

* Values are based on triplicate analysis

TABLE 8: Selective solid phase preconcentration of heavy metal from drinking tap water

Alumina phase	Sample volume	Metal ion	$ng\ ml^{-1}$ Spiked	$\mu g\ L^{-1}$ Detected	Percent extraction
100-mg(I)	1.0 L	Fe(III)	5.097	0.890	$87.3 \pm 2\%$
100-mg(I)	1.0 L	Fe(III)	1.005	0.180	$89.6 \pm 2\%$
100-mg(II)	1.0 L	Pb(II)	4.900	0.970	$99.0 \pm 2\%$
100-mg(II)	1.0 L	Pb(II)	1.056	0.210	$99.4 \pm 3\%$
100-mg(III)	1.0 L	Cr(III)	5.160	1.001	$97.0 \pm 2\%$
100-mg(III)	1.0 L	Cr(III)	1.120	0.220	$98.2 \pm 4\%$

* Values are based on triplicate analysis

Phase(II) was found to give also excellent percentage recovery value(97.0%) for the removal of Pb(II) from waste water sample

Selective solid phase preconcentration of heavy metal from drinking tap water by modified alumina phases(I-III)

TABLE 8 summarizes the results of selective metal extraction and preconcentration of Fe(III), Cr(III) and Pb(II) by newly modified alumina phases(I-III) via micro-column applications using 5.0ml concentrated nitric acid as a preconcentration reagent and with a preconcentration factor of 200. One can conclude that excellent preconcentration values of the spiked concentration(1.056-4.900 ng ml^{-1}) of Pb(II) by modified neutral alumina phase(II) judging from the determined percentage recovery values(99.0-99.4±2-3%). Preconcentration of the spiked concentration of Cr(III) (1.120-5.160 ng ml^{-1}) by modified basic alumina phase(III) was also found to establish excellent percentage recovery values(97.0-98.2±2-4%). Finally, the preconcentration recovery of spiked concentration(1.005-5.097ng ml^{-1}) of Fe(III) by modified acidic alumina phase(I) giving percentage values of 87.0-89.6±2-3%.

CONCLUSION

The organic modifier used in this study, methionine, is characterized by its property as being friendly to the environments. The experimental method and steps used to load methionine on the surface of alumina phases required only water and ethanol as reaction solvents and these two compounds are also friendly to the environments. Thus, the materials and methods applied in this study clearly refer to clean and green chemistry. In addition the outlined and described results confirm the potential applications of newly modified alumina phases(I-III) for selective extraction, removal and preconcentration of heavy metal ions from real waste and drinking water samples.

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