April 2008 Volume 4 Issue 1

Trade Science Inc.

Macromolecules

An Indian Journal

Full Paper

MMAIJ, 4(1), 2008 [29-39]

Solid phase extraction and preconcentration of lead and other heavy metals by alumina phases-functionalized-dithizone as chelating inorganic ion exchangers

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Received: 24th September, 2007 ; Accepted: 29th September, 2007

ABSTRACT

Dithizone, a chelating compound, was immobilized on the surface of three different types of alumina, acidic, neutral and basic, via physical adsorption as a simple, direct, efficient and environment friendly technique. Surface characterization of the newly modified alumina-functionalized-dithizone (I-III) was accomplished by 70-eV EI-MS as a promising technique for surface and thermal evaluations as well as infrared analysis and determination of the surface coverage values. The metal interaction properties of the newly modified alumina phases were studied for a series of heavy metal ions via determination of metal capacity under the influence of various factors. The results of distribution coefficient and separation factor revealed that the newly modified alumina phases are highly selective for Pb(II) and Cr(III). The potential suitability and applicability of modified alumina phases as solid chelating ion exchangers, extractors and preconcentrators for Pb(II) from real water and waste water samples were successfully accomplished with percentage removal, extraction and recovery values in the range of 93.0±6.0%-99.6±4.0% and a preconcentration factor equals 200 and without any interference of the matrix effect.

KEYWORDS

Alumina;
Dithizone;
Selective extraction;
Preconcentration;
Waste water.

INTRODUCTION

Alumina is known as one of the most commonly used inorganic solid supports and come after silica gel for their analytical chemistry applications. Alumina types are widely used due to their presence in various varieties with basic differences in their chemical and physical properties[1-2]. Commercial alumina is prepared by heating alumina trihydrate, $Al_2O_3.3H_2O$ and the products are known to compose of aluminum oxide, Al_2O_3, alumina monohydrate Al_2O_3. H_2O. In general, most of the surface water molecules are present in the form of surface hydroxyl groups or adsorbed water. Based on the pH-value of aqueous suspension of alumina, three types of alumina could be classified[3]. Acidic alumina with a characteristic pH-value of aqueous suspension equal 4.0±0.5, neutral alumina(pH of aqueous suspension =7.0±0.5) and basic alumina type with a characteristic pH-value of aqueous suspension equal 9.5± 0.5. However, the surface of alumina as an example of inorganic solid supports is characterized by the presence of certain functional groups as hydroxyl ones in different arrangements and distribution[4,5].

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 determinations, 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 the 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[6-8]. 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. The hydroxyl groups on the surface of alumina are the major contributing factors that are responsible for binding, adsorption, and extraction processes. The weak ion exchange properties of these hydroxyl groups are to favor their low interaction behavior with various species[3-6]. Therefore, improvements of the adsorption efficiency and extraction power of the SPE as well as incorporation of certain selectivity characters are always aimed via surface modification with certain functional groups. Functionalized chelating inorganic solid supports are the most important types of sorbents that can be used and applied in the processes of solid phase extraction of toxic and non-toxic transition and non-transition metal ions due to the presence of certain donor atoms, mainly nitrogen, oxygen, sulfur and phosphorus in these compounds leading to incorporation of certain selectivity characters into the newly modified SPE.

Different techniques are usually used to modify and characterize alumina surface for the improvement of their analytical and adsorptive characteristics. 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 inorganofunctiona lization, in which the group anchored on the surface may be an organometallic or a metallic oxide[9,10]. The second type of surface modification of alumina phases is usually performed via surfactant coating followed by direct immobilization of the modifier of interest either organic or inorganic and commonly used for synthesis and formation of newly modified alumina phases[11,12]. 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[13,14]. Modification of alumina phases with organic or inorganic modifiers can be accomplished by physical adsorption approach via thermal or hydrothermal treatment. This approach is very simple compared to other methods and considered to be 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 or electrostatic interaction or hydrogen bond formation or any other type of interaction[15].

Diphenylthiocarbazone(dithizone)is one of the chemical reagents that experienced with great interests as a sulfur and nitrogen donor atoms containing chelating compound in various approaches for design and synthesis of chemically or physically loaded sorbents. Dithizone-modified-sorbents were found to be widely applied as excellent extractants for heavy metal ions and their species from different matrices[16-18]. The immobilization of dithizone on the surface of alumina phases is limited[19]. However, immobilization of dithizone on the surface of different types of alumina, acidic neutral and basic, via physical adsorption technique as a simple, direct, efficient and environment friendly approach is aimed for the sake of preparation of newly modified alumina phases that are capable of binding, extraction, separation and preconcentration of toxic and hazardous species from aqueous samples.

EXPERIMENTAL

Chemical and reagents

Three alumina types of standard specifications (150mesh, 58Å, and surface area=155m^2/g) were purchased from Aldrich Chemical Company, USA. The first type is an acidic alumina with a pH value of 4.5±0.5 for the aqueous suspension. The second alumina type is neutral with an assigned pH 7.0±0.5 of aqueous suspension and the third alumina phase is a basic type with a pH value of 9.5±0.5.

Diphenylthiocarbazone(dithizone, Formula weight= 256.33) purchased from BDH Limited, Poole, England and used as received.

Solutions

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

Instrumentation

Infrared spectra of the modified 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. Thermolyne 47900 furnace was used to determine the mmol g^{-1} surface coverage values of modified alumina phase via thermal desorption analysis. 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, chelating compound 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. The mass spectral sheets were computerized to give I/Base and its corresponding mass.

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

Diphenylthiocarbazone(dithizone), 2.6g(~10.1 mmol), as the organic modifier was weighed and transferred to a 500ml conical flask and completely dissolved by heating at ~50^{0}C in 400ml of ethyl alcohol. To this solution 10.0±0.1g of alumina phase, either acidic, neutral or basic, was added and the reaction mixture was further stirred at this temperature for six hours. The newly modified alumina phases were filtered, washed with 50ml ethyl alcohol on three portions and finally with 50ml of diethyl ether. Alumina phases were then allowed to dry in an oven at 60^{0}C.

Surface coverage determination

The determination of surface coverage values of modified alumina phases (I-III) was accomplished by thermal desorption method[3,20]. In this method, 100±1mg of the 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^{0}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 sample was transferred to a desiccator and left to reach the room temperature. The weight loss of the organic chelating compounds was determined by the 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-dithizone.

Stability test of the newly synthesized alumina phases (I-III) in different acidic buffer solutions

0.5g of the modified alumina phase was mixed with 50ml 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. 25.0±1mg of the buffered alumina phase was added to a solution containing 9.0 ml of buffer solution (pH=6) and 1.0ml of 0.1 molar of Cu(II). The mixture was automatically shaken for 30 minutes by an automatic shaker and the degree of hydrolysis of alumina phase-physically adsorbed-dithizone in different buffer solutions was determined from the metal uptake values of Cu(II).

Determination of metal capacity

The metal capacity values (μmol g^{-1}) of the modified alumina phases (I-III) for the extraction of 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) in various buffer solutions (pH 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0) were determined in triplicate by the batch equilibrium technique. In this method, 50±1 mg of the dry phase was weighed and added to a mixture of 1.0ml of 0.1M metal ion and 9.0ml of the selected buffer solution into a 50ml measuring flask. These flasks were then 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. Of the dry alumina phase, 50±1mg were added to a mixture of 1.0ml of 0.1M of each metal ion and 9.0 ml 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 following metal ions were used to prepare the solutions used to determine the distribution coefficient values of the various modified alumina phases (I-III). The 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 1.0ppm 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 the metal ion was completed to 50ml by using 5% hydrochloric 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

The following water samples were collected and used to conduct this study[21-23]. Waste water samples were collected from Damnhour drug factory and spiked with ~1.0-2.0ppm 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 500mg of the selected modified alumina phase with a flow rate 10.0ml min^{-1}. The effluent solution was collected and acidified with hydrochloric 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 ruining 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[24,25]

Preconcentration of Pb(II) was performed according to this procedure. 1.0 liter of drinking tap water sample was spiked with (~1.0 and 5.0ng/ml $^{-1}$) of the target metal ion. This water sample was passed over a preconcentration micro-column packed with 500 mg-modified alumina phase(I-III) with a flow rate of (~10.0ml min^{-1}) under air pressure. The adsorbed metal ion on the alumina surface was desorbed by the flow of 5.0 ml of concentrated nitric acid and determined by atomic absorption analysis to identify the percentage recovery and preconcentration values.

RESULTS AND DISCUSSION

1. Surface characterization of alumina phases-physically adsorbed-dithizone (I-III)

Electron impact mass spectrometric analysis

Mass spectrometry technique is one of the powerful analytical methods of analysis for qualitative and quantitative determination of organic and inorganic compounds[26]. It can be applied for the identification of products formation as well as study the reaction follow-up. Several techniques are usually used to apply the sample for introduction into the mass spectrometer and the ionization chamber. The most commonly used sample application methods are the direct insertion probe (DIP). 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 temperature = 300°C. The possible application of EI-MS as a potential technique for identification of surface modification is aimed as well as the information that can be generated about the thermal stability of the newly modified alumina phases. Finally, the presentation of further evidence for the possible use and application of these modified or some of these modified phases as new stationary phases for gas chromatography because the suitable GC-phases must be thermally stable over a wide range of temperature either used in isothermal or temperature programming systems[27,28].

The 70-eV electron impact-mass spectra(70-eV EI-MS) determined by the direct insertion probe(DIP) and heated to 300-350^{0}C as a maximum heating temperature for the alumina phases-physically adsorbed-dithizone(I-III) was performed for modified acidic, neutral and basic alumina phases (I-III). The mass spectrum of dithizone and blank acidic alumina phase were also studied for comparison. It was found that two characteristic low masses at m/z 18 and 44 are the major peaks in the mass spectrum of acidic alumina phase. The peak at m/z 18 is mainly due to the presence of either adsorbed water molecules on the surface of blank acidic alumina phase or to the presence of water molecules inside the ionization chamber of the mass spectrometer. The latter attribution is assisted by the presence of the mass spectrum peak at m/z 44 which corresponds to the presence of CO_2 molecules[28,29]. No other characteristic fragment ion peaks could be identified from the mass spectrum of blank acidic alumina phase. The 70-eV EI-MS-DIP spectrum of dithizone as an organic modifier was characterized by the presence of two peaks that are related to the molecular ion peak at m/z 254(84%) and 256(8%). Some other fragment ion peaks are derived and related to the dithizone moiety at m/z 105(65%) for the formation of this fragment ion$[\Phi\text{-N=N}]^+$, 92(86%) for the fragment ion$[\Phi\text{-NH}]^+$, 77(100%) as the base peak and due to the phenyl ring. The 70-eV EI-MS-DIP spectrum of acidic alumina-physically adsorbed-alumina phase (I) is identified by the presence of these masses at m/z 18, 28 and 44 that correspond 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 dithizone on the surface of acidic alumina(4.48 %) which is calculated from the surface coverage of phase (I). No molecular ion peak at m/z 256 was detected but other identified fragment ions at m/z 105(9 %), 92 (6 %) and 77(1 %) as described.

The same trend 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 3.64 and 4.15%, respectively. However, the molecular ion peak at m/z 256 was identified in the 70-eV EI-MS of phases(II) and(III) with relative abundance <2%. 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 confirmation of surface adsorption of dithizone on either neutral or basic alumina phases. The thermal stability of these newly modified alumina phases can be confirmed due to the absence of good mass fragment patterns in these phases as compared to the 70-eV EI-MS-DIP spectrum of dithizone.

Infrared spectrophotometric analysis of modified alumina phases (I-III)

The infrared spectrum of blank unmodified alumina phases were identified by the presence of three infrared peaks at 3600-3400, 1650 and 1000-400cm^{-1} that are mainly due to the alumina matrix. However, immobilization of dithizone on the surface of either acidic, neutral or basic alumina can lead to exhibition of few infrared peaks that correspond to the immobilized chelating compound. These peaks are expected to be weak or very weak ones depending on the percentage of loaded dithizone on the surface of alumina phase. These values are 4.48% for modified acidic alumina(I), 3.64% for modified neutral alumina (II) and 4.15% for modified basic alumina(III). The characteristic infrared peaks in the infrared spectra of newly modified alumina phases-physically adsorbed-dithizone (I-III) were found to be centered at 1440, 1570, 3095 and 3440cm^{-1} corresponding to, ν-N=N, ν-C=S, ν-C-H (aromatic) and ν-N-H functional groups respectively.

Determination of the surface coverage values of modified alumina phases(I-III)

The surface coverage values of the newly modified alumina phases-physically adsorbed-dithizone (I-III) were determined by thermal desorption method and metal probe testing method. The determined surface coverage values on the basis of thermal desorption method were found 0.175mmol/g^{-1} for newly modified acidic alumina-physically adsorbed-dithizone (I), 0.142mmol/g^{-1} for newly modified neutral alumina-physically adsorbed-dithizone (II) and 0.162mmol/g^{-1} for newly modified basic alumina-physically adsorbed-dithizone (III). These values were also translated into percentage coverage of dithizone on the surface of alumina phases and found to be 4.48%, 3.64% and 4.15% for modified alumina phases (I), (II) and (III), respectively. These values confirm the possible binding via adsorption of dithizone on the surface of either acidic or neutral or basic alumina type. The closeness in these surface coverage values for modified alumina phases (I-III) proves that there is no role for the pH values of the blank unmodified acidic, neutral and basic alumina phases in the process of physical adsorption.

In the metal probe testing method the highest bound metal to the surface of newly modified phase, as determined and evaluated by the metal capacity value, is usually taken as a representative value for the surface coverage value of this modified phase. According to this method the estimated surface coverage mmol/g^{-1} value for modified acidic alumina phase-physically adsorbed-dithizone (I) was found to be 0.440mmol/g^{-1} based on the value of metal capacity of Cu(II). The surface coverage of newly modified neutral alumina phases-physically adsorbed-dithizone (II) was found to be 0.460 mmol/g^{-1} as identified from the metal capacity values of either Cr(III) or Cu(II) with this modified alumina phase. 0.460mmol/g^{-1} was found to be the surface coverage of newly modified basic alumina phase-physically adsorbed-dithizone(III)as identified from the metal capacity values of both Cr(III) and Cu(II) with the modified basic alumina (III). The reason for such high surface coverage determination by this method may be attributed to the contribution of the alumina matrix via the ion exchange characters incorporated into these types of solid supports[3,10]. The same trend and argument can also be confirmed for the insignificant contribution of the acidic-basic characters of blank alumina phases in the adsorption process of dithizone on their surfaces.

TABLE 1 compiles the calculated and evaluated surface coverage values of the three newly modified alumina phases-physically adsorbed-dithizone (I-III) as determined by the thermal desorption and related percentage coverage values as well as those determine by the metal probe testing methods. The pH-values of the blank unmodified alumina and modified alumina phases (I-III) are also listed in TABLE 1.

2. Stability of alumina phases-physically adsorbed-dithizone (I-III) in different buffer solutions

The stability of newly modified alumina phases-physically adsorbed-dithizone (I-III) was studied in different buffer solutions (pH 1-7) to identify the stability of the organic chelating modifier, dithizone, on the surface of each alumina phase. The hydrolyzed alumina phase was then used to determine the mmol g^{-1} of Cu(II) which was found to exhibit the maximum metal uptake value within all tested metal ions. 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 alu-

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

Alumina Phase	pH-value	Thermal desorption mmol g^{-1}	Pecentage coverage	Metal probe mmol g^{-1}
Blank acidic alumina	4.4	------	-------	------
Blank neutal alumina	6.7	------	-------	------
Blank basic alumina	8.9	------	-------	------
Modified alumina (I)	3.8	0.175	4.48 %	0.440
Modified alumina (II)	4.1	0.142	3.64 %	0.460
Modified alumina (III)	6.8	0.162	4.15 %	0.460

TABLE 2 : Percentage stability of modified alumina phases (I-III).

pH	Alumina phase (I) % stability (μmol g^{-1})	Alumina phase (II) % stability (μmol g^{-1})	Alumina phase (III) % stability (μmol g^{-1})
1.0	300 (68.2 %)	340 (73.9 %)	280(65.2 %)
2.0	320 (72.7 %)	340 (73.9 %)	360 (78.3 %)
3.0	320 (72.7 %)	300 (65.2 %)	380(82.6 %)
4.0	300 (68.2 %)	300(65.2 %)	300 (65.2 %)
5.0	300 (68.2 %)	300 (65.2 %)	300(65.2 %)
6.0	300 (68.2 %)	300 (65.2 %)	300 (65.2 %)
7.0	340(77.3 %)	320 (69.6 %)	300(65.2 %)

TABLE 3 : Metal capacity (μmol g^{-1}) of alumina phase (I) in buffer solutions (pH 5.0 -7.0)*

Metal ion	Phase (I)		
	pH 5.0	pH 6.0	pH 7.0
Mg(II)	00	00	00
Ca(II)	10	00	00
Cr(III)	60	250	350
Mn(II)	00	00	00
Fe(III)*	20	40	40
Co(II)	00	00	00
Ni(II)	00	20	20
Cu(II)	50	140	440
Zn(II)	20	30	40
Cd(II)	00	00	00
Hg(II)	00	20	40
Pb(II)	20	40	130

*Metal capacity values of Fe(III) in pH 2, 3 and 4.

TABLE 4 : Metal capacity (μmol g^{-1}) of alumina phase (II) in buffer solutions (pH 5 -7)*

Metal ion	Phase (II)		
	pH 5.0	pH 6.0	pH 7.0
Mg(II)	00	00	00
Ca(II)	00	00	00
Cr(III)	120	230	460
Mn(II)	00	00	00
Fe(III)*	40	50	40
Co(II)	00	00	00
Ni(II)	00	20	30
Cu(II)	50	160	460
Zn(II)	20	30	40
Cd(II)	00	00	00
Hg(II)	00	20	60
Pb(II)	10	80	130

*Metal capacity values of Fe(III) in pH 2, 3 and 4.

mina phase in the tested buffer solutions. TABLE 2 compiles the results obtained for stability of modified alumina phases-physically adsorbed-dithizone (I-III) towards hydrolysis and leaching process. It is evident from the data given in TABLE 2 that acidic alumina phase-physically adsorbed-dithizone (I) is highly stable in neutral buffer solution with pH 7 giving a percentage stability value of 77.3%, while in most of the other tested buffer solutions the percentage stability values were in the range of 68.2-72.7 %. On the other hand, neutral alumina phase-physically adsorbed-dithizone (II) was found to give almost the same percentage stability value of 65.2 % in the buffer solutions of pH 3.0-6.0. The highest percentage stability value (73.9 %) of phase (II) was identified in lower acidic buffer solutions with pH 1-2. Basic alumina phase-physically adsorbed-dithizone (III) was found to give the highest percentage stability value (82.6 %) in buffer solution with pH 3.0 and the other percentage values were identified in the range 65.2-78.3 %.

3. Metal Capacity values of alumina phases-physically adsorbed-dithizone (I-III)

Effect of the pH-value on the metal capacity of modified alumina phases (I-III)

TABLES 3-5 compile the determined metal capacity values for binding of each metal ion, expressed in μmol g^{-1} in buffer solutions with pH 5-7. It is evident from the data given in TABLE 3 for the newly modified alumina phase (I) that Cr(III) and Cu(II) are the highest extracted metal ions in buffer solutions pH 5.0-7.0. The maximum metal capacity value of Cr(III) was found to be 350 μmol g^{-1} as the highest extracted and bound to modified alumina phase in buffer solution of pH 7.0. For Cu(II), the maximum metal capacity value determined for phase (I) was found to correspond to 440μmol/g^{-1} in buffer solution of pH 7.0. 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.

TABLE 4 compiles the metal capacity values determined by the newly modified neutral alumina phase (II). Phase (II) was found to exhibit similar behavior

TABLE 5 : Metal capacity (μmol g^{-1}) of alumina phase (III) in buffer solutions (pH 5 -7)*

Metal ion	Phase (III)		
	pH 5.0	pH 6.0	pH 7.0
Mg(II)	00	00	00
Ca(II)	00	00	00
Cr(III)	170	250	460
Mn(II)	00	00	00
Fe(III)*	40	40	40
Co(II)	00	10	10
Ni(II)	00	20	30
Cu(II)	50	140	460
Zn(II)	20	30	40
Cd(II)	00	00	00
Hg(II)	00	20	80
Pb(II)	20	80	140

*Metal capacity values of Fe(III) in pH 2, 3 and 4.

and trend with phase (I). Cu(II) and Cr(III) were found to give the highest metal capacity values in buffer solutions pH 7.0 with a metal capacity of 460µmol g^{-1}. Cr(III) is the highest extracted and bound metal ion to modified alumina phase (II) in buffer solution, pH 6.0 based on the determined metal capacity value (460µmol g^{-1}). The determined metal capacity values of Pb(II) by the newly modified neutral alumina phase-physically adsorbed-dithizone (II) were found 10, 80, 130µmol g^{-1} in buffer solutions, pH 5.0, 6.0 and 7.0, respectively. These values along with other metal capacity values, as the case of Cr(III) and Cu(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.

TABLE 5 compiles the metal capacity values in µmol g^{-1} for the same series of metal ions in various buffer solution (pH 5.0-7.0) except the values of Fe(III) were determined in buffer solutions 2.0, 3.0 and 4.0. It is easy to figure out that newly modified alumina phase(III) is similarly behaving as the previously discussed modified alumina phases (I) and (II) toward binding and extraction of the tested metal ions especially, Cr(III), Fe(III) Cu(II), Zn(II) and Pb(II).

The following outlines may be listed as the conclusions from the study of the buffer effect on the determined metal capacity values by phases (I-III) and summarized as follows:

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

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

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

(IV) The effect of pH values of the contact solution on the determined metal capacity values is clear for highly extracted metal ions, Cr(III), Cu(II) and Pb(II).

3. Effect of shaking time on the metal capacity values determined by the batch equilibrium technique

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 the metal capacity values by the newly modified alumina phases-physically adsorbed-dithizone (I-III).

Three metal ions, Cu(III), Cr(III) and Pb(II), were selected to perform the effect of shaking time values (1, 5,10,15,20,25 and 30 minutes) on the metal capacity values of these metal ions and this study is represented by figures 1-3. It clear from figure 3 that Pb(II) was similarly behaving toward extraction by the three newly modified alumina phases(I-III). Very close percentage extraction values can be observed under the identical shaking time by the newly modified alumina phases (I-III). In other words, Pb(II) was found to show percentage extraction values of ~75% when only 5-minutes shaking time was used. This time shows also that fast equilibration of Pb(II) with either alumina phase (I), (II) or (III) can be attained.

The same trends, observations, arguments and con-

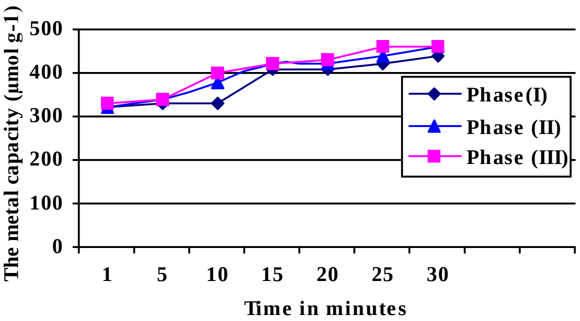

Figure 1 : Effect of shaking time on the metal capacity of Cu(II) by modified alumina phases (I-III)

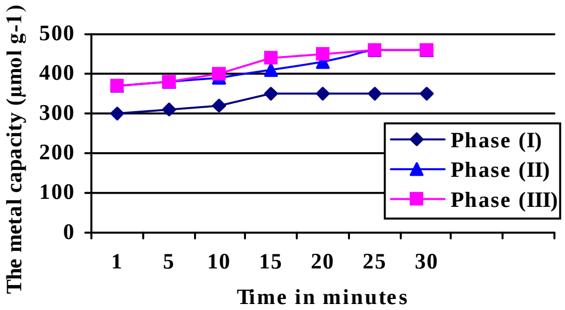

Figure 2 : Effect of shaking time on the metal capacity of Cr(III) by modified alumina phases (I-III)

clusions can be outlined for the extraction of Cu(II) and C(III) by the newly modified alumina phases (I-III) as shown in figures 1 and 2, respectively.

4. Distribution coefficient values of metal ions by alumina phases-physically adsorbed-dithizone (I-III)

The distribution coefficient values for the modified alumina phase-physically adsorbed-dithizone (I-III) are given in TABLE 6. It is evident that surface modification of alumina phases with dithizone as an organic chelating modifier has led to change the chemical properties of acidic alumina surface toward binding and extraction with certain metal ions[3]. It is also clear from the data given in TABLE 6 that Fe(III), Pb(II) and Cr(III) are highly extracted by modified acidic alumina phase (I) based on their K_d values 3388, 1410, and 1083, respectively. The other tested metal ions were found to exhibit low distribution values by the modified acidic alumina (I) and these include Mg(II), Ca(II), Cd(II), Zn(II), Ni(II), Co(II), Mn(II) and Cu(II). This conclusion can be confirmed by evaluation of the separation factors for these tested metal ions. Thus the order for increasing the distribution coefficient values for the tested metal ions by alumina phase (I) can be arranged in the following order:

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

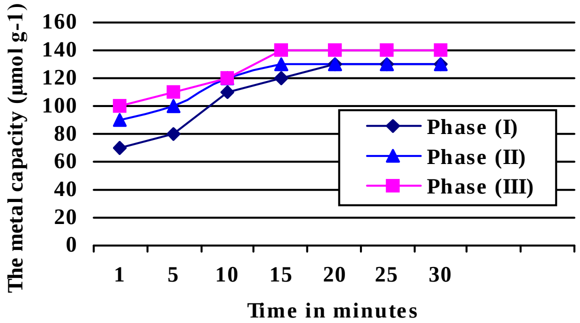

Figure 3 : Effect of shaking time on the metal capacity of Pb(II) by modified alumina phases (I-III)

TABLE 6 : Distribution coefficient values for the various metal ions by modified alumina phase (I-III).

Metal ion	Phase (I)	Phase (II)	Phase (III)
Mg(II)	116	141	198
Ca(II)	255	456	966
Cr(III)	1083	2740	58200
Mn(II)	76	964	1872
Fe(III)	3388	2536	5374
Co(II)	156	1600	1834
Ni(II)	105	1905	3865
Cu(II)	161	2172	30540
Zn(II)	462	771	3856
Cd(II)	375	1674	6010
Pb(II)	1410	88920	179800

The distribution coefficient values for the modified neutral alumina phase-physically adsorbed-dithizone (II) are listed in TABLE 6. It is evident that Pb(II) is the highest extracted metal ion by modified alumina phase (II) based on the K_d values 88020. Thus, the order for increasing the distribution coefficient values for the tested metal ions by alumina phase (II) can be arranged as follows:

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

The distribution coefficient values for the modified basic alumina phase-physically adsorbed-dithizone (III) are also listed in Table 6. In the manner, Pb(II) is the highest extracted metal ion by modified basic alumina phase (III) based on the K_d value=179800. 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), Zn(II), 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 phase (III) can be outlined in the following order:

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

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

The separation factor αA/B for Pb(II), Fe(III) and Cr(III) versus other tested metal ions by the newly modified acidic alumina phase (I) are shown and represented in figure 4. It is clear from the data shown that Pb(II) can be selectively extracted from all metal ions except Fe(III) and Cr(III) owing to low separation factors of Pb(II) versus these two metal ions as shown in figure 4.

Figure 5 represents the separation factor of Pb(II) versus other tested metal ions by modified neutral alumina-physically adsorbed-dithizone phase (II). It is evident from figure 5 that Pb(II) can be selectively extracted from all other metal ions without any possible interference from any metal ion owing to the high sepa-

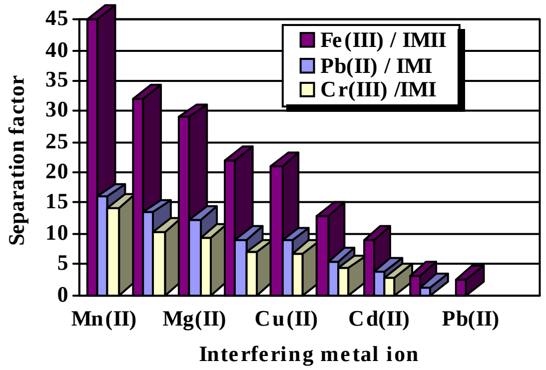

Figure 4: Separation factors of Fe(III), Pb(II)& Cr(III) versus other Interfering Metal ions (IMI) by phase(I)

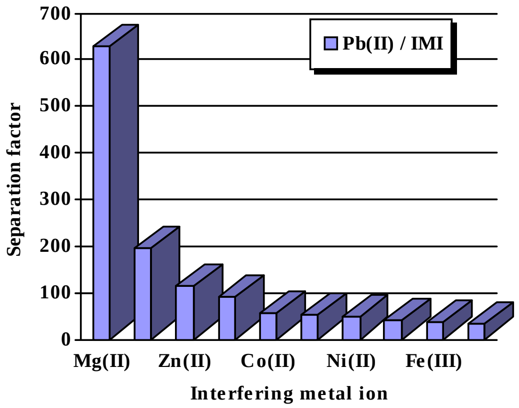

Figure 5: Separation factors of Pb(II) versus other interfering metal ions (IMI) by phase(II)

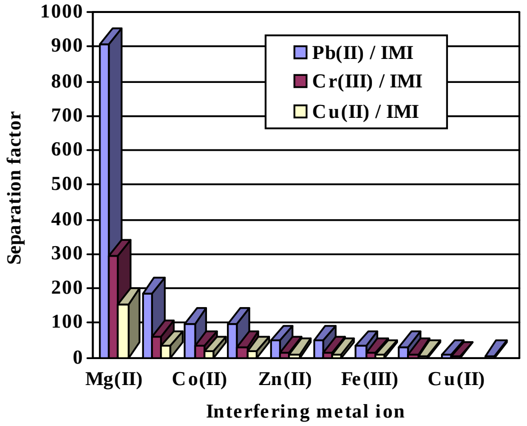

Figure 6: Separation factors of Pb(II), Cr(III) & Cu(II) versus other interfering metal ions (IM) by phase(III)

TABLE 7 : Selective solid phase extraction and removal of Pb(II) from waste water samples

Alumina phase	Sample volume	Metal ion	μg ml^{-1} spiked	μg ml^{-1} detected	Percent extraction*
500-mg (I)	L	Pb(II)	1.8055	0.0217	98.8±3.0 %
500-mg (II)	L	Pb(II)	2.1168	0.1164	94.5±5.0 %
500-mg (III)	1.0 L	Pb(II)	2.2359	0.0089	99.6±4.0 %

*Values are based on triplicate analysis

ration factors of Pb(II) versus other metal ions.

The separation factor $\alpha_{A/B}$ for Pb(II), Cr(III) and Cu(II) versus other tested metal ions by modified basic alumina phase (III) are shown and represented in Figure 6. It is clear from the data shown that Pb(II) and Cr(III) can be selectively extracted from other interfering metal ions as Mg(II), Ca(II), Co(II), Mn(II), Zn(II), Ni(II), Fe(III) and Cd(II).

6. Selective solid phase extraction, removal and preconcentration of Pb(II) from water samples by alumina phases (I-III)

Alumina phases-physically adsorbed-dithizone were identified and characterized by incorporated high selectivity characters towards heavy metal ions as Pb(II). The high toxicity of lead to human being caused by lead poisoning is well known and reported. Lead toxicity inactivate enzymes related to haem synthesis giving rise to accumulation of haem precursors and anemia as well as renal tubular dysfunction manifesting with impaired tubular reabsorption of glucose, amino-acids and phosphate[31]. Therefore, strong needs for preconcentration of Pb(II) from different matrices and samples are always aimed and directed by the utilization of modified solid sorbents[32]. This study part is devoted to evaluate the potential applications of newly synthesized alumina phases for selective extraction, removal and preconcentration of pb(II) from real water samples. TABLE 7 summarizes the results of selective metal extraction and removal of Pb(II) from waste water collected from Damnhour drug factory by modified alumina phases(I-III)) via micro-column application. It is evident from the percentage extraction values given in TABLE 7 that excellent extraction of Pb(II) by the newly modified alumina phase (I) was achieved with percentage recovery values of 98.8±3.0% based on triplicate analysis. Phase (II) was also found to give also an excellent percentage recovery value for the selective extraction and removal of Pb(II) (94.5±5.0%) from the waste water sample. Application of alumina phase-physically adsorbed-dithizone (III) was also proved to give excellent results for the removal of Pb(II) from waste water sample providing percentage recovery values of 99.6±4.0 % for the tested metal ion.

TABLE 8 summarizes the results of selective solid preconcentration of lead ion by alumina phases-physi-

TABLE 8 : Selective solid phase preconcentration of Pb(II) from drinking tap water by alumina phases (I-III).

Alumina phase	Sample volume	Preconcentration reagent	Metal ion	Preconcentration factor	ng ml^{-1} spiked	μg ml^{-1} detected	Percent recovery*
100 -mg (I)	L	5 ml conc. HNO_3	Pb(II)	200	4.800	0.893	93.0±6 %
100 -mg (II)	1.0 L	5 ml conc. HNO_3	Pb(II)	200	4.800	0.922	96.0±5%
100-mg (III)	1.0 L	5 ml conc. HNO_3	Pb(II)	200	4.800	0.912	95.0±8%
100 -mg (I)	1.0 L	5 ml conc. HNO_3	Pb(II)	200	0.960	0.183	95.0±4 %
100 -mg (II)	1.0 L	5 ml conc. HNO_3	Pb(II)	200	0.960	0.186	97.0±6 %
100-mg (III)	1.0 L	5 ml conc. HNO_3	Pb(II)	200	0.960	0.188	98.0±3 %

*Values are based on triplicate analysis

cally adsorbed-dithizone(I-III) via micro-column application. From the data given in TABLE 8 one can conclude that excellent percentage recovery values (93.0-98.0±3.0-6.0%) were established for preconcentration of 1.0 and ~5.0ng/ml^{-1} of Pb(II) by modified neutral alumina phase(I-III). The results of these studies proved the capability and suitability of newly modified alumina phases-physically adsorbed-dithizone for selective extraction, removal and preconcentration of Pb(II) from real water samples.

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