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Implementation of Hybrid Inorganic/Organic Adsorbents for Removal and Preconcentration of Heavy Metals from Industrial Waste and Drinking Waters

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Three hybrid inorganic/organic adsorbents based on alumina and phenylazoformic acid 2-phenylhydrazide were synthesized, characterized and examined for their heavy metal sorption properties. The main purpose of this research paper is to study and explore the combined hybrid characters of inorganic/organic sorbents for the selective removal and preconcentration of heavy metals via static and dynamic solid phase techniques from industrial wastewater and drinking tap water samples as well. The hybrid inorganic/organic adsorbents were identified as strongly resistive to leaching in solutions with pH 1–7 and thermally stable up to 350°C. Optimization of heavy metal removal by implementation of newly designed hybrid inorganic/organic adsorbents was studied in presence of various factors as the effect of pH of contact solution and reaction time via determination of the metal sorption capacity and distribution coefficient. The hybrid adsorbents were successfully implemented for the selective removal of Pb(II), Cu(II), Fe(III), and Cr(III) from industrial wastewater samples with recovery values in the range of 91–99 ± 2–3% as well as 98–99 ± 1–3% for the selective preconcentration of Pb(II), Cu(II), and Cr(III) from drinking tap water samples without noticeable interference caused by the matrix effect.

Keywords alumina; heavy metals; hybrid adsorbents; phenylazoformic acid 2-phenylhydrazide; preconcentration; removal

INTRODUCTION

Heavy metals are dangerous species owing to their bioaccumulation in biological organisms. Damage of the mental and central nervous system as well as function alterations in blood composition, lungs, kidneys, and liver are some diseases caused by the bioaccumulation of heavy metals in human bodies (1). Heavy metal toxicity may result from contaminated drinking water, or intake via the food chain. Contamination of water supplies by heavy metals may be a result of industrial wastewater disposal, human waste, or even from releasing heavy metals by soils into streams, lakes, rivers, and groundwater via acid rain (2). The presence of toxic heavy metal ions, compounds, or species in the aquatic systems or other environmental samples poses serious health risks and environmental threats that forced the scientific researchers under pressure to imperatively address, solve and develop new extraction, removal, and preconcentration methods and techniques to efficiently and economically detect, eliminate, and purify high and low concentration levels of these toxic contaminants from drinking water, wastewaters, as well as various water matrices (3,4).

Chemical precipitation, membrane process, ion exchange, electro-deposition, and adsorption techniques were reported as the traditional methods for heavy metals removal, extraction, purification, preconcentration, and treatment from various water matrices. However, the chemical precipitation processes are known for production of great undesired amounts of mud, while ion exchangers and membrane separation are considered as high cost procedures. The surface adsorption technique has been found as one of the most important and efficient approach for heavy metals treatments in the third world countries owing to the possible easy operation, affordable cost and resulting high water quality (5–7).

Adsorption is mainly based on the utilization of solid adsorbents that originate from either biological based materials, organic components or, inorganic constituents (8,9). Biological materials, known as biosorbents, are widely used and implemented for heavy metal removal from various water matrices and these include fungi (10), algae (11), seaweeds (12,13), microorganisms (14,15), agriculture materials (16) and several biopolymers (17,18). Organic adsorbents applied for heavy metal removal via adsorption are usually accomplished by the applications of polymeric ion exchangers in which the binding and interaction of metal species with these adsorbents is favored via ion exchange mechanism or by applications of chelating polymers whereas the target metal ions are directly attached to these kinds of adsorbents via chelation or complex formation mechanism (19–24).

Inorganic adsorbents are mainly characterized by their high mechanical and thermal properties as well as excellent

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metal adsorption capacity as compared to other biosorbents or organic adsorbents. Inorganic adsorbents are generally based on metal oxides in the form of free or hybrid composition. Among them are aluminum oxide (25) silicon oxide (26), iron (III) oxide, zirconium (IV) oxide, iron (III)-zirconium (IV) hybrid oxide, and iron (III)-aluminum (III) mixed oxide (27). Inorganic-organic hybrids are those materials derived from the combination and union of inorganic solid sorbents with organic compounds for the formation of new adsorbents. These are characterized by carrying multi-functional characters that are directly related to their building unites and further implemented in heavy metal removal from their matrices (28). Alumina and silica are among the most commonly used inorganic components for the formation of hybrid adsorbents based on surface chemisorption or physisorption of the organic counter part (29,30). Hybrid inorganic-organic materials based on combination of alumina matrix with chelating compounds were recently found as excellent adsorbents for heavy metal removal, purification, extraction, separation and preconcentration (31–36) as well as speciation (37–39) from various water samples.

The purpose of the present study is directed toward examination and evaluation the bi-functionality incorporated into three hybrid inorganic-organic adsorbents synthesized on the basis of direct immobilization of phenylazoformic acid 2-phenylhydrazide as an excellent chelating organic compound with nitrogen and oxygen donor atoms (40,41) on the surface of various acidic-basic alumina matrices. The feasibility of these hybrid adsorbents was investigated and explored in the light of their capability and selectivity for removal and preconcentration of heavy metal ions such as lead (II), chromium (III) and copper (II) as well as other heavy metals from industrial wastewater and drinking tap water samples by static and dynamic techniques.

EXPERIMENTAL

Chemical and Reagents

Phenylazoformic acid 2-phenylhydrazide (Formula weight = 240.27 and melting point = 156°C) was purchased from Aldrich Chemical Company and used as received. Three alumina types of standard specifications (150 mesh, 58 A°, and surface area = 155 m^2/g) were purchased from Aldrich Chemicals Company, USA. The first type is an acidic alumina with assigned pH value of aqueous suspension of 4.5 ± 0.5. The second alumina type is neutral with an assigned pH of aqueous suspension of 7.0 ± 0.5 and the third alumina type is a basic type with a pH value of 9.5 ± 0.5. The three alumina types were 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 selected metal salts are lead (II) acetate trihydrate, copper (II) chloride dihydrate, chromium (III) chloride hexahydrate, nichel (II) chloride hexahydrate, magnesium (II) chloride hexahydrate, zinc (II) chloride, cobalt (II) chloride hexahydrate, cadmium (II) chloride, iron (III) chloride hexahydrate, calcuim chloride dihydrate, manganese (II) chloride tetrahydrate, and mercury (II) chloride. The metal solutions were prepared from doubly distilled water (DDW).

Synthesis of Hybrid Alumina-Phenylazoformic Acid 2-Phenyl-Hydrazide Adsorbents (I–III)

Phenylazoformic acid 2-phenylhydrazide (Diphenylcarbazone) (2.4 g; ~10.0 mmol) was weighed and transferred to a 250 ml conical flask. A mixture of 100 ml of toluene and 50 ml of ethyl alcohol was then added to this sample and allowed to stir on cold until complete dissolution of phenylazoformic acid 2-phenylhydrazide. To this solution 10.0 ± 0.1 g of either acidic, neutral or basic alumina type was added and the reaction mixture was further stirred for four hours. The newly synthesized hybrid alumina-phenylazoformic acid 2-phenylhydrazide adsorbents (I–III) were filtered, washed with 50 ml toluene three times, 50 ml ethyl alcohol, and finally with 50 ml of diethyl ether. Hybrid alumina adsorbents (I–III) were then allowed to dry in an oven adjusted to 60°C for eight hours.

Stability of the Newly Synthesized Hybrid Adsorbents (I–III)

A sample of hybrid alumina adsorbents (50 ± 1 mg) was mixed with 20 ml of the selected buffer solutions (pH 1–7) in a 100 ml volumetric flask and automatically shaken for one hour. The mixture was filtered and dried at 70°C. Buffered alumina adsorbent (25.0 ± 1 mg) was added to a solution containing 9.0 ml of buffer solution (pH = 7) and 1.0 ml of 0.1 molar of Cu(II). The mixture was automatically shaken for 30 minutes and the degree of hydrolysis of hybrid alumina adsorbent in different buffer solutions was determined from the metal uptake values of Cu(II).

Instrumentation

Infrared spectra of the hybrid alumina adsorbents (I–III) were recorded from KBr pellets using a Perkin-Elmer spectrophotometer, model 1430. Measurements of the pH of metal ions and buffer solutions were carried out with an Orion 420. The pH-meter was calibrated against standard buffer solutions with pH 4.0 and 9.2. Thermal desorption analysis was accomplished by using a Thermolyne 47900 furnace. The electron impact mass spectra of blank alumina, phenylazoformic acid 2-phenylhydrazide, and hybrid alumina adsorbents (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. Determination of the metal concentration was performed by using a Perkin-Elmer model 2380 atomic absorption spectrophotometer and a SHIMADZU model AA-6650 Atomic absorption spectrophotometer at the standard wavelength and working range for each tested metal ion.

Determination of Surface Coverage

The determination of the surface coverage values of hybrid alumina adsorbents (I–III) was accomplished by the thermal desorption method. In this method, 100 ± 1 mg of the dry alumina adsorbent was weighed and ignited at 550°C in a muffle furnace. The initial temperature was set at 50°C and gradually increased to 550°C in about 20 minutes. The ignited adsorbent was then kept at this temperature for one hour and left to cool down inside the furnace till 70°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 sample weights before and after the process of thermal desorption. Blank samples of alumina adsorbents were also subjected to the same thermal desorption procedure as described for comparison with the results obtained for hybrid alumina adsorbents.

Determination of Metal Sorption Capacity

Effect of pH Value on the Metal Sorption Capacity

The metal sorption capacity values ($\mu mol\,g^{-1}$) of the hybrid alumina adsorbents (I–III) for 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 solutions (pH 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, and 1.0 M sodium acetate) were determined in triplicate by the batch equilibrium technique. In this method, 50 ± 1 mg of the dry alumina adsorbent was weighed and added to a mixture of 1.0 ml of 0.1 M metal ion and 9.0 ml of the selected buffer solution into 50 ml 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 100 ml of doubly-distilled water. The unbounded metal ion by the studied hybrid alumina adsorbent was subjected to complexometric titration using 0.01 M EDTA solution or by the atomic absorption analysis.

Effect of Shaking Time on the Metal Sorption Capacity

The effect of shaking time intervals (5, 10, 15, 20, 25, and 30 minutes) on metal sorption capacity and the percentage of the extraction was also studied for some selected metal ions by the batch equilibrium technique according to the following procedure. Dry alumina adsorbent, 50 ± 1 mg, was added to a mixture of 1.0 ml of 0.1 M of each metal ion and 9.0 ml of buffer solution, which was found to exhibit the highest metal capacity in the previous section. This mixture was filtered, washed with 100 ml DDW, and the unextarcted metal ion by hybrid alumina adsorbent was determined by complexometric EDTA titration.

Determination of the Distribution Coefficient

The following metal ions were selected for the determination of the distribution coefficient values of hybrid alumina adsorbents (I–III). These are 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). The concentration of each metal ion solution is $\sim 1.0\,\mu g\,ml^{-1}$. In a 25 ml measuring flask, 100 mg ± 1 mg of the hybrid alumina adsorbent was weighed, 10 ml of $1.0\,\mu g\,ml^{-1}$ metal ion was then added and the flask was shaken by an automatic shaker for 1-hour. This mixture was filtered in a 50 ml measuring flask and washed with 10 ml DDW. The volume of metal ion was completed to 50 ml by using 5% hydrochloric acid solution. A standard solution of the metal ion was prepared by mixing 10 ml of $1.0\,\mu g\,ml^{-1}$ metal ion solution and 10 ml of DDW. The volume of this metal ion was completed to 50 ml by 5% HCl solution. A blank solution was also prepared from 20 ml DDW and 30 ml of 5% HCl solution. The concentrations of metal ions in sample, standard and blank solutions were determined by atomic absorption analysis.

Implementation of Hybrid Alumina Adsorbents (I–III) for Selective Removal and Extraction of Heavy Metal Ions from Industrial Waste and Drinking Tap Water Samples

The following water samples were collected and used to conduct this study. Industrial wastewater samples collected from Extracted Oil Company-Damanhour Factory and used for the extraction of Pb(II), Cu(II), Fe(III) and Cr(III) via micro-column application. The first industrial wastewater sample (1.0 liter) was spiked with ~ 1.0–$2.0\,\mu g\,ml^{-1}$ of Cu(II) and Fe(III) and extracted by hybrid acidic alumina adsorbent (I). The second wastewater sample (1.0 liter) was spiked with ~ 1.0–$2.0\,\mu g\,ml^{-1}$ of Cr(III) and Pb(II) and this sample was extracted by hybrid neutral alumina adsorbent (II). The third wastewater sample was used to examine hybrid basic alumina adsorbent (III) for selective removal of the spiked ~ 1.0–$2.0\,\mu g\,ml^{-1}$ concentration of Cr(III) and Pb(II).

The extraction procedure of these metal ions was performed by running the prepared industrial wastewater samples over a micro-column packed with 500 mg of the selected alumina adsorbent with a flow rate of $10\,ml\,min^{-1}$. The effluent solution was collected and acidified with hydrochloric acid and subjected for atomic absorption spectrophotometric analysis of the free metal ions. Industrial wastewater samples were also subjected for atomic absorption spectrophotometric analysis for each specific metal ion before running over the column.

Preconcentration of Heavy Metals from Drinking Tap Water Samples

Pre-concentration of heavy metal ions was performed according to this procedure. Cu(II) was selectively preconcentrated from water samples by hybrid alumina adsorbent (I), while, Cr(III) and Pb(II) were selectively preconcentrated from drinking tap water samples by hybrid alumina adsorbents (II) and (III), respectively. 1.0 liter sample of drinking tap water was spiked with ($\sim$5.0 ng ml^{-1}) of selected metal ions. The water sample was passed over a micro column packed with 100 mg-hybrid alumina adsorbent (I–III) with a flow rate of (10.0 ml min^{-1}) under air pressure. The extracted metal ions on the surface of the alumina was desorbed by the flow of 5.0 ml of concentrated HNO_3 and determined by atomic absorption analysis.

RESULTS AND DISCUSSION

Surface Characterization of Hybrid Alumina-Phenylazoformic Acid 2-Phenylhydrazide Adsorbents (I–III)

Determination of the Surface Coverage Values

The surface coverage values of hybrid alumina-phenylazoformic acid 2-phenylhydrazide adsorbents (I–III) were determined by thermal desorption method. The determined surface coverage values based on this method were found to be 0.218, 0.203, and 0.227 mmol g^{-1} for hybrid alumina adsorbents (I), (II) and (III), respectively. These values confirm the possible binding via adsorption of phenylazoformic acid 2-phenylhydrazide on the surface of either acidic, neutral, or basic alumina type. The closeness in the surface coverage mmol g^{-1} values for these hybrid alumina adsorbents reveals that there is no role for the pH values of blank acidic, neutral, and basic alumina types in enhancing the physical adsorption process of the organic modifier. The measured pH values of the aqueous suspension of hybrid alumina adsorbents (I), (II), and (III) were found as 4.1, 5.6, and 6.3, respectively.

Infrared of Hybrid Alumina Adsorbents (I–III)

The infrared spectra of hybrid alumina adsorbents (I–III) were studied and compared with their blank analogues. The infrared spectra of blank unmodified alumina are characterized by the presence of three infrared peaks at 3600–3400, 1650, and 1000–400 cm^{-1} that are mainly due to the alumina matrix (37,38). However, surface impregnation of the organic modifier, phenylazoformic acid 2-phenylhydrazide, on either acidic, neutral or basic alumina can lead to exhibition of few infrared peaks that correspond to the immobilized chelating compound. The characteristic infrared spectra of immobilized phenylazoformic acid 2-phenylhydrazide were found to produce weak peaks at 1750, 1429, 1310, 3300, and 3100 cm^{-1} corresponding to $\nu_{C=O}$, $\nu_{N=N}$, ν_{C-N}, ν_{N-H}, and aromatic moieties, respectively. The ν_{N-H} at 3300 was overlapped by the peak corresponding to ν_{O-H} at 3600–3400 cm^{-1}. The mode of binding of phenylazoformic acid 2-phenylhydrazide to the surface of acidic, neutral or basic alumina adsorbents may be in the form of hydrogen bonding between surface hydroxyl groups and nitrogen or oxygen donor atoms of the organic modifier. In addition, binding may be produced via adsorption of oppositely charged species of the organic modifier and alumina matrix. Figure 1 shows the FT-IR spectrum of hybrid basic alumina adsorbent.

Stability of Hybrid Alumina Adsorbents (I–III)

Stability in Buffer Solutions

The stability of newly modified hybrid alumina adsorbents (I–III) in various buffer solutions (pH 1–7) was tested to identify the possible degree of leaching of phenylazoformic acid 2-phenylhydrazide from the surface of hybrid alumina adsorbents (I–III). The hydrolyzed alumina adsorbent was then used to determine the µmol g^{-1} of Cu(II) as one of the highest extracted metal ions by hybrid alumina adsorbents (I–III). The values of determined µmol g^{-1} for the hydrolyzed alumina were compared with those of the untreated alumina to calculate the percentage of stability for each alumina adsorbent in the tested buffer solutions. Figure 2 is a direct representation of the determined µmol g^{-1} stability percentage values. It is evident that neutral and basic hybrid alumina adsorbents (II) and (III) are not affected by buffer solutions (pH 1–7) based on exhibition of perfect percentage stability values of 100.0%. Acidic hybrid alumina adsorbents (I) was found to retain its surface coverage values with a 100.0%-stability value in buffer solution with pH 3.0, 4.0, and 5.0 while in lower pH solutions, pH 1.0 and 2.0, the percentage stability value was found to be $\sim$65%. Therefore, as shown in Fig. 2, the three newly synthesized hybrid alumina adsorbents (I–III) are characterized by high stability to leaching processes.

Thermal Stability by EI-MS

Thermal stability of hybrid alumina adsorbents (I–III) was studied and evaluated by direct insertion probe (DIP) at 350°C and 70-eV electron impact-mass spectra (70-eV EI-MS). The mass spectra of blank acidic, neutral and basic alumina adsorbents as well as phenylazoformic acid 2-phenylhydrazide were studied and compared with hybrid alumina adsorbents (I–III). The mass spectrum of blank acidic alumina adsorbent showed two characteristic low masses at m/z 18 and 44 as the major peaks (37–39). A peak at m/z 18 is mainly due to the presence of either adsorbed water molecules on the surface of blank acidic alumina adsorbent or water molecules inside the ionization chamber of the mass spectrometer. The latter attribution is assisted by the presence of mass peak at m/z 44 which

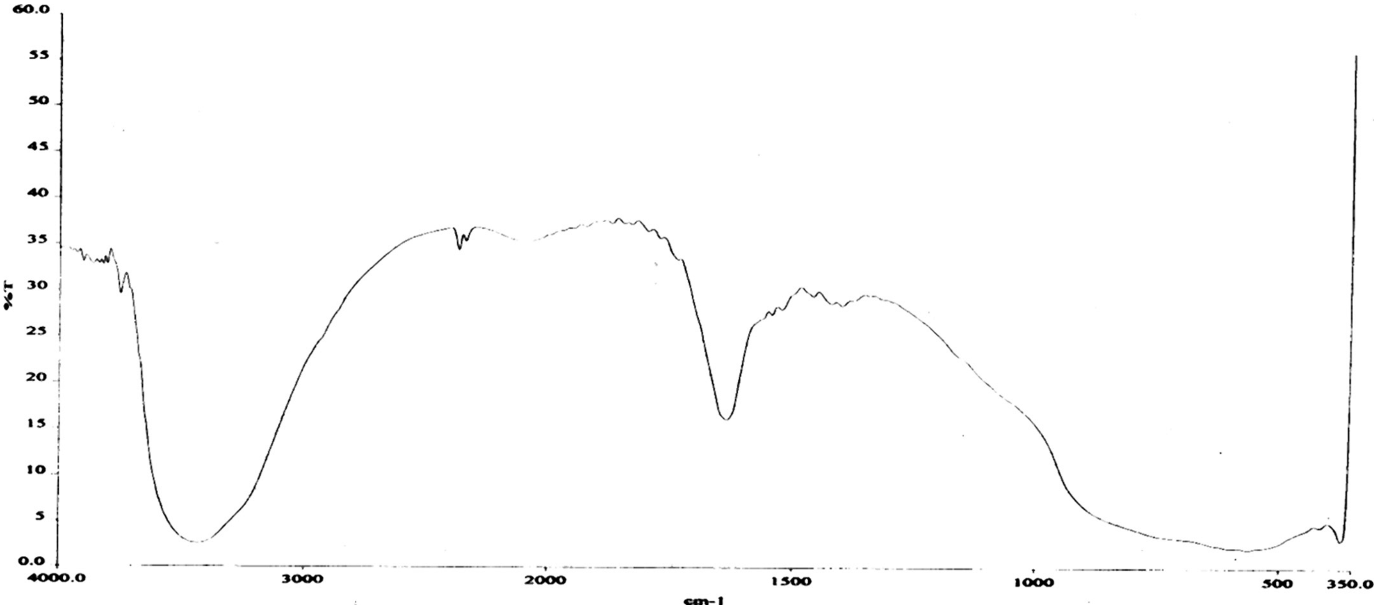


FIG. 1. FT-IR spectrum of hybrid alumina (II).

corresponds to the presence of CO_2 molecules. No other characteristic fragment ion peaks could be identified from the mass spectrum of blank alumina. The EI-MS of pure phenylazoformic acid 2-phenylhydrazide was found to exhibit several characteristic fragment ions peaks. A peak at m/z 240 (43%) represents the molecular ion of phenylazoformic acid 2-phenylhydrazide. Other fragment ions were also identified at m/z 135 (72%) $[\Phi{-}NH{-}NHCO]^+$, 107 (76%) $[\Phi{-}NH{-}NH]^+$, 105 (28%) $[\Phi{-}N{=}N]^+$, 92 (86%) $[\Phi{-}NH]^+$, and 77 (100%) as the base peak for the phenyl fragment ion. The 70-eV EI-MS-DIP spectrum of hybrid acidic alumina adsorbents (I) showed few fragment peaks at m/z 135 (9%), 105 (3%), and 92 (8%). The same trends and observation can also be identified and outlined from the 70-eV EI-MS-DIP spectra of hybrid neutral and basic alumina adsorbents (II) and (III), respectively. The conclusion that can be drawn from the thermal stability as studied and evaluated by the mass spectrometric evaluation of these hybrid alumina adsorbents is the strong adsorption of phenylazoformic acid 2-phenylhydrazide on the surface of either acidic, neutral or basic alumina as well as the expected advantageous thermal stability of these

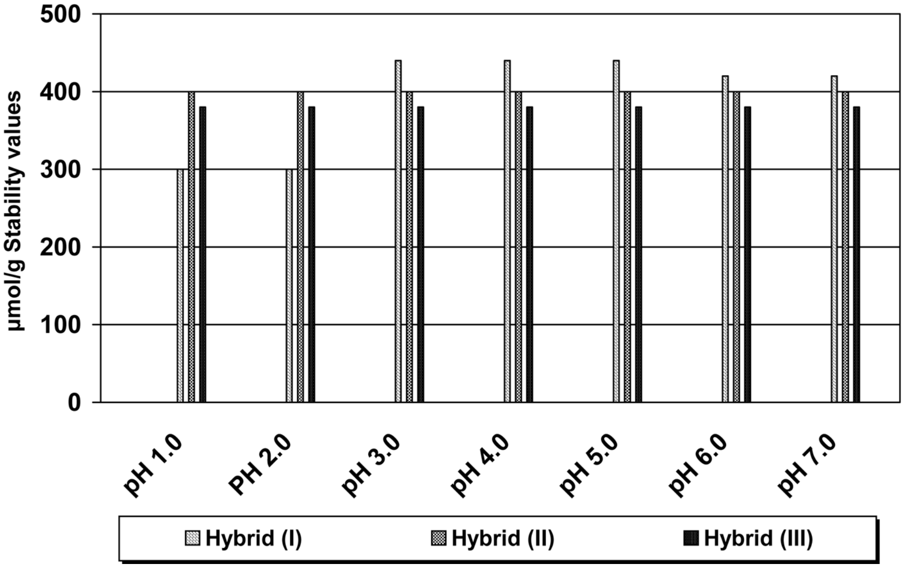


FIG. 2. Stability of hybrid alumina adsorbents (I–III) in buffer solutions.

newly synthesized hybrid alumina adsorbents (I–III) due to the low percentage values of the detected fragment ion peaks. Figures 3 a, b, and c show the EI-MS-DIP of blank basic alumina, phenylazoformic acid 2-phenylhydrazide and hybrid alumina (III), respectively.

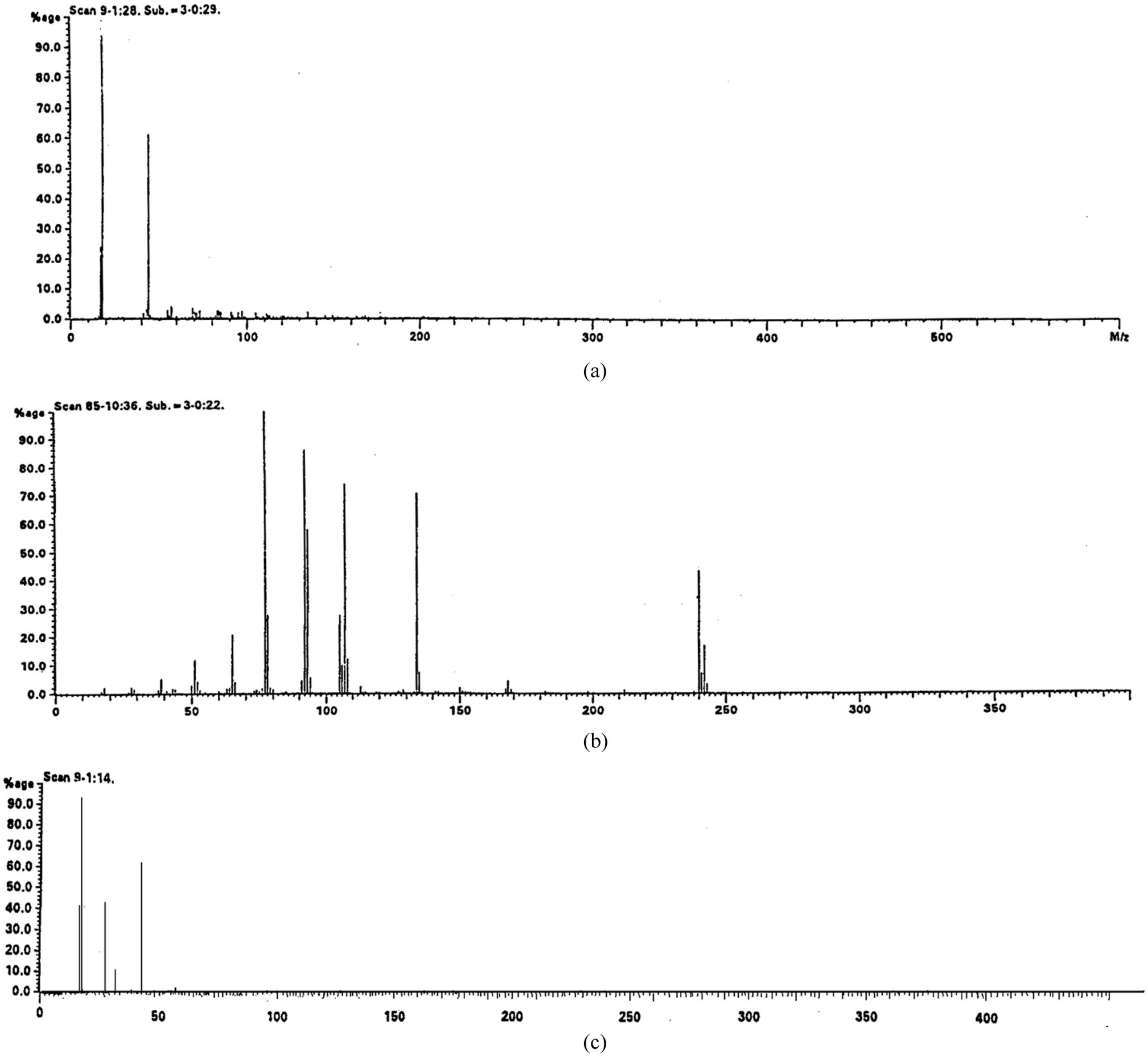
Sorption Properties of Hybrid Alumina Adsorbents (I–III)

Effect of pH on Metal Sorption Capacity

The metal sorption capacity (MC_t) at any time, expressed in $\mu mol\,g^{-1}$, can be calculated from Eq. (1).

$$MC_t = \frac{(C_0 - C_t)V_{ml}}{Mass_g} \times 1000 \qquad (1)$$

Where C_0 and C_t are the initial and final metal ion concentrations in solution expressed in $mol\,l^{-1}$. V_{ml} is the volume of metal ion solution expressed in ml and $Mass_g$ is the mass of adsorbent expressed in gram. The effect of pH of tested metal ion solutions on the amount extracted by hybrid alumina adsorbents is considered as the major important factor in such procedure because of the ability of most metal ions to be strongly influenced by free or immobilized chelating compound as phenylazoformic acid 2-phenyl-hydrazide at certain pH values. The maximum determined metal capacity values, expressed in $\mu mol\,g^{-1}$, for the tested metal ions along with the optimum pH values for binding of each metal ion are compiled in Table 1 and the overall data of this study are represented in Figs. 4–6.



(a)

(b)

(c)

FIG. 3. EI-MS-DIP of (a) blank basic alumina, (b) phenylazoformic acid 2-phenylhydrazide and (c) hybrid alumina (III).

TABLE 1
Maximum metal sorption capacity values (μmol g^{-1}) in optimum buffer solutions

	Hybrid (I)		Hybrid (II)		Hybrid (III)	
Metal ion	μmol g^{-1}	pH	μmol g^{-1}	pH	μmol g^{-1}	pH
Mg(II)	00	1–7	00	1–7	00	1–7
Ca(II)	00	1–7	00	1–7	00	3–7
Cr(III)	**250**	**6–7**	**250**	**6–7**	**250**	**6–7**
Mn(II)	00	1–7	00	1–7	00	1–7
Fe(III)	100	4	80	4	80	4
Co(II)	00	1–7	00	1–7	00	1–7
Ni(II)	10	7	30	7	30	7
Cu(II)	**440**	7	**400**	**7**	**380**	7
Zn(II)	30	7	40	7	40	7
Cd(II)	30	7	00	1–7	00	1–7
Hg(II)	120	7	150	7	**170**	**1–7**
Pb(II)	**200**	**7**	**240**	**7**	**270**	**7**

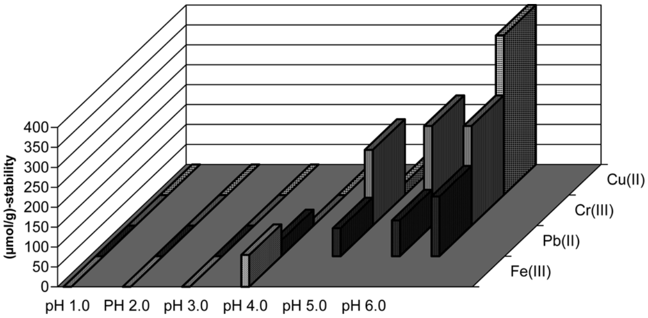


FIG. 5. Effect of pH on metal sorption capacity values of hybrid neutral alumina adsorbent (II).

It is evident from the given metal sorption capacity values that buffer solution with a pH 7 is the optimum buffering condition for forcing maximum binding and extraction processes between hybrid alumina adsorbents (I–III) and most metal ions as Cr(III), Cu(II), Hg(II), and Pb(II). On the other hand, Mg(II), Ca(II), Co(II), Ni(II), Zn(II), and Cd(II) were found to show little tendency to bind with hybrid alumina adsorbents (I–III) judging from the determined metal sorption capacity values for these metal ions (0–40 μmol g^{-1}). The pH value of the contact solution was also found to show no effect in such binding and extraction process for these low metal capacity species. However, the maximum determined metal capacity values were found to correspond to Cu(II) with a value of 440, 400 and 380 μmol g^{-1} for hybrid alumina adsorbents (I), (II), and (III), respectively. In addition, it is also evident from the data of metal capacity values listed in Table 1 that most of the tested metal ions were found to exhibit similar binding properties with the three hybrid alumina adsorbents (I–III). For example, Cr(III) was found to give the same maximum metal capacity values (250 μmol g^{-1}) with alumina adsorbents. Close individual metal capacity values of Fe(III) and Pb(II) were found for the three tested hybrid alumina adsorbents and these were characterized in the range (100–80 μmol g^{-1}) and (200–270 μmol g^{-1}), respectively. Thus, one can conclude from these outlined results that acidic-basic characters of hybrid alumina adsorbents (I–III) have no role in directing the metal capacity towards either one and this conclusion proves the suitability and equal efficiency of any hybrid alumina adsorbent either, acidic or neutral or basic for use and application in metal ion extraction and separation. This conclusion can also be confirmed from the following increasing orders for the tested metal ions by the newly synthesized hybrid alumina adsorbents (I–III).

For hybrid alumina (I), the order is: Mg(II) = Ca(II) = Mn(II) = Co(II) < Ni(II) < Zn(II) = Cd(II) < Fe(III) < Hg(II) < Pb(II) < Cr(III) < Cu(II).

For hybrid alumina (II), the order is: Mg(II) = Ca(II) = Mn(II) = Co(II) = Cd(II) < Ni(II) < Zn(II) < Fe(III) < Hg(II) < Pb(II) < Cr(III) < Cu(II).

For hybrid alumina (III), the order is: Mg(II) = Ca(II) = Mn(II) = Co(II) = Cd(II) < Ni(II) < Zn(II) < Fe(III) < Hg(II) < Pb(II) < Cr(III) < Cu(II).

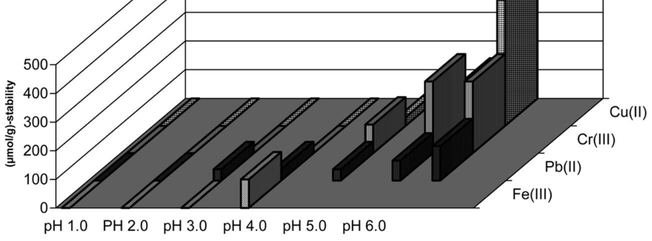


FIG. 4. Effect of pH on metal sorption capacity values of hybrid acidic alumina adsorbent (I).

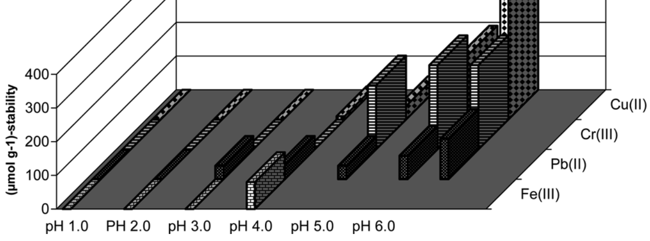


FIG. 6. Effect of pH on metal sorption capacity values of hybrid basic alumina adsorbent (III).

Effect of Shaking Time on the Metal Sorption Capacity

The effect of selected shaking time values (1, 5, 10, 15, 20, 25, and 30 minutes) on the determined metal capacity values of Pb(II) and Cu(II) by the three hybrid alumina adsorbents (I–III) was studied and evaluated. Figure 7 is a simple representation of the behavior of hybrid alumina adsorbents toward binding and extraction with the two studied metal ions. It is clear that 5-minutes shaking time was found to be a sufficient time for >75% extraction of the tested metal ions referring to the fast equilibration and kinetics between the two tested metal ions and hybrid alumina adsorbents. For example, the percentage extraction of Cu(II) after 5-minutes shaking time was found to be 87%, 98%, and 100% for hybrid alumina adsorbents (I), (II), and (III), respectively. In a similar fashion, Pb(II) was also found to give good percentage extraction values. The close metal capacity values or percentage extraction values give good evidence that there is no superiority of any alumina adsorbent in the kinetics of extraction process for these metal ions, but the superiority of hybrid alumina adsorbents (I–III) is only related to the value of metal sorption as previously discussed.

Distribution Coefficient Values

The distribution coefficient value is calculated from the following Equation (2):

$$K_d, \text{ml g}^{-1} = \frac{C_{\text{i,ex}}(\mu\text{g g}^{-1})}{C_{\text{i,sol}}(\mu\text{g ml}^{-1})} \qquad (2)$$

Where, $C_{\text{i,ex}}$ and $C_{\text{i,sol}}$ are the concentration values of the surface-bound metal ion and solution-free metal ion, respectively. The distribution coefficient values for hybrid alumina-phenylazoformic acid 2-phenyl- hydrazide adsorbents (I–III) are given in Table 2. It is evident from the data given that Fe(III) and Cu(II) are highly extracted by hybrid acidic alumina adsorbent (I) giving K_d values of 17410 and 9800 for the two metal ions, respectively. The hybrid neutral alumina adsorbent (II) was found to show high selectivity characters for Pb(II), Cu(II) and Fe(III) with K_d values of 78810, 18320, and 13350, respectively. The highest determined K_d values by hybrid basic alumina adsorbent (III) were found to correspond to Pb(II) ($K_d = 78810$) and Cr(III) ($K_d = 58200$). The contribution of the alumina matrix may be considered to account for such high selective extraction of metal ions based on their high determined distribution coefficient values.

TABLE 2
Distribution coefficient values of metal ions by hybrid alumina adsorbents (I–III)

Metal ion	Hybrid (I)	Hybrid (II)	Hybrid (III)
Mg(II)	16	309	386
Ca(II)	240	462	913
Cr(III)	1700	4615	**58200**
Mn(II)	630	1505	2005
Fe(III)	**17410**	**13350**	18950
Co(II)	575	3836	4500
Ni(II)	280	2964	6450
Cu(II)	**9800**	**18320**	**19900**
Zn(II)	49	4838	6705
Cd(II)	268	1270	11350
Pb(II)	**2307**	**78810**	**78810**

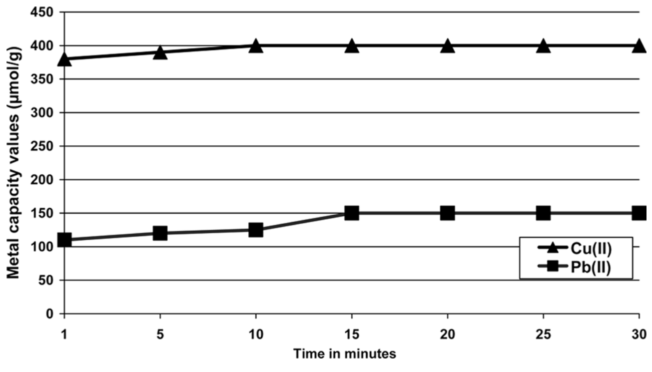


FIG. 7. Effect of shaking time on the metal capacity values of Cu(II) and Pb(II) by hybrid neutral alumina adsorbent (II).

A comparison of the results obtained by determination of the metal sorption capacity versus distribution coefficient refers to the following points. From the metal sorption capacity point of view, one can easily conclude first that when the concentration levels of examined metal ions are high in the mol l^{-1} or mmol l^{-1} range, the three studied hybrid alumina adsorbents (I–III) are similar in their metal up-take and sorption properties (Fe(III) < Cr(III) < Cu(II)). Second, the same orders of affinity and selectivity toward various tested metal ions were elucidated regardless of the mmol g^{-1} sorption capacity values. Third, the effect of pH values of hybrid alumina adsorbents (I–III) is showing insignificant difference between these adsorbents. Fourth, the surface loaded phenylazoformic acid 2-phenylhydrazide is well characterized as the only effective and reacting species with interacting metal ions without any significant role of the alumina matrix. On the other hand, when dealing with low concentration levels of metal ions ($\mu\text{g ml}^{-1}$ or ng ml^{-1}) as in the case of distribution coefficient determination, the following points are apparent. First, hybrid alumina adsorbents (I) was differently behaving giving this order Fe(III) > Cu(III) > Pb(II), while neutral alumina adsorbent (II) was identified by showing the metal order Pb(II) > Cu(II) > Fe(III) and hybrid basic alumina adsorbent (III) was characterized by giving this order Pb(II) > Cr(III) > Cu(II) indicating different behaviors of these adsorbents. Second, the order of distribution coefficient values increases from hybrid acidic alumina (I) to hybrid neutral alumina (II) to hybrid basic alumina (III) referring to the strong influence and role of the pH values of tested adsorbents in which low concentration levels of metals are existing and favoring the strong binding with higher pH value of hybrid alumina matrix. Third, phenylazoformic acid 2-phenylhydrazide as the surface organic chelating compound was found to contribute less in the case of distribution coefficient determination, while the most contributing species in this study is related to the alumina matrix either an acidic, neutral or basic. Such difference in metal binding behaviors is mainly attributed to various adsorption mechanisms that control metal interaction with surface active groups. In the case of high metal concentration, possible complex formation mechanism is considered between donor atoms and acceptor metal ions. In the case of low levels of metal concentration, an ion exchange process may be favored. Thus, the conclusion that can be drawn from this comparative study refers to the necessity of performing both studies, distribution coefficient and metal sorption capacity, for an accurate and practical evaluation of the affinity and selectivity characters incorporated into hybrid alumina adsorbents for removal of toxic heavy metals.

Implementation of Hybrid Alumina Adsorbents (I–III) in Selective Removal and Preconcentration of Heavy Metals

Toxic heavy metals such as lead, chromium, copper, mercury, and cadmium are excessively released into the environment due to rapid industrialization and often detected in untreated industrial wastewaters. Removal of these toxic species from industrial wastewaters by the adsorption technique, known as one of the most effective physico-chemical treatment processes, is always planned and aimed. Therefore, the following section is directed and devoted toward extraction and removal of heavy metal ions such as Cr(III), Cu(II), and Pb(II) from wastewater samples collected from extracted oil factory.

Table 3 summarizes the results of implementation of hybrid alumina adsorbents (I–III) for selective removal and extraction of heavy metals such as Cr(III), Fe(III), Cu(II), and Pb(II) from industrial wastewater samples (Extracted Oil Company-Damanhour Factory) via microcolumn separation. It is evident from the values listed in Table 3 that hybrid basic alumina adsorbent (III) was found to give excellent percentage recovery values of 99% and 95% for the spiked concentration of 2.285 and 1.066 $\mathrm{mg l^{-1}}$ of Pb(II) and Cr(III), respectively. The determined percentage recovery values of Pb(II) and Cr(III) were found to correspond to 93% and 95%, respectively when hybrid neutral alumina adsorbent (II) was implemented. Hybrid acidic alumina adsorbent (I) exhibited also excellent selective extraction results for the tested heavy metal ions from wastewater samples giving the percentage extraction values of 92% and 91% for Cu(II) and Fe(III), respectively. One can easily identify that the three hybrid alumina adsorbents (I–III) are experienced with excellent recovery values for the removal of the examined heavy metal ions without possible interference of the matrix effect caused by the presence of dissolved organic and inorganic species in the industrial wastewater samples.

TABLE 3
Implementation of hybrid alumina adsorbents (I–III) in selective removal of heavy metals from industrial wastewater samples

Hybrid alumina	Metal ion	$\mathrm{mg\,l^{-1}}$ spiked	$\mathrm{mg\,l^{-1}}$ detected	Percent extraction*
500-mg (III)	Pb(II)	2.285	0.002	99 ± 2%
	Cr(III)	1.066	0.052	95 ± 3%
500-mg (II)	Pb(II)	2.082	0.139	93 ± 2%
	Cr(III)	1.129	0.050	95 ± 2%
500-mg (I)	Cu(II)	1.773	0.155	92 ± 2%
	Fe(III)	1.118	0.100	91 ± 3%

*Values are based on triplicate analysis.

The determination of extremely low concentration levels of elements mainly requires initial procedures for selective removal, separation and preconcentration. Implementation of an appropriate extraction and preconcentration techniques are always known as the direct solution to increase the concentration of target metal ions, improve sensitivity of the instrumentation and remove co-existing species that interfere in the detection process (42–44). The preconcentration technique, also known as enrichment, is usually used to increase analyte/matrix ratio in which the analyte is transferred into a new experimentally acceptable phase for analytical determination and evaluation. Atomic absorption spectrophotometry (AAS) is widely used as the most commonly available analytical technique for determination of metal ions, species and metallic contaminants in a wide range of environmental matrices providing a combination of the analytical advantages with low operational cost. However, AAS determination of trace metallic ions, species, or compounds in environmental samples such as water are always faced by the low concentration levels of these components as well as other undesired interfering species caused by the matrix composition and leading to what is called the matrix effect. Therefore, an efficient and simple preconcentration approach must be implemented for the removal and detection of low concentration levels of heavy metals in water samples.

Table 4 summarizes the results of selective preconcentration of Cu(II), Cr(III) and Pb(II) from drinking tap water samples by hybrid alumina adsorbents (I), (II), and (III),

TABLE 4
Implementation of hybrid alumina adsorbents (I–III) in selective preconcentration of heavy metals from drinking tap water samples

Hybrid alumina	Sample volume	Metal ion	$ng\,ml^{-1}$ spiked	$\mu g\,ml^{-1}$ detected	Percent extraction*
100 mg (III)	1.0 L	Pb(II)	4.800	0.940	98 ± 3%
100 mg (II)	1.0 L	Cr(III)	5.420	1.080	99 ± 3%
100 mg (I)	1.0 L	Cu(II)	4.920	0.980	99 ± 1%

*Values are based on triplicate analysis.

respectively via a preconcentration micro-column application. A preconcentration factor equal 200 was established on the basis of using 5 ml concentrated HNO_3 as a preconcentration reagent. One can conclude that excellent percentage recovery value (99 ± 1–3%) was established for the preconcentration of Cu(II) and Cr (III) by hybrid acidic alumina adsorbent (I) and hybrid neutral alumina adsorbent (II), respectively. A value of 98 ± 3% was identified as the percentage recovery of the spiked concentration (4.800 $ng\,ml^{-1}$) of Pb(II) by hybrid basic alumina adsorbent (III). The results outlined in this section for the implementation of newly synthesized hybrid alumina adsorbents (I–III) for selective preconcentration of heavy metals from drinking tap water refer to the excellent recovery values without possible interference of the matrix effect.

CONCLUSION

The designed hybrid inorganic/organic alumina/phenylazoformic acid 2-phenylhydrazide adsorbents were found highly efficient and selective when implemented for purification of industrial waste and drinking tap water samples from heavy metals without any matrix effect caused by the interference of co-existing organic or inorganic species. Hybrid alumina adsorbents were also identified by their high resistance to thermal decomposition as well as strong stability toward acid leaching. The role played by alumina matrix either an acidic, neutral, or basic in metal binding processes is only dominant when the concentration levels of metal ions are low and in the range of microgram per milliliter or less while the contribution of surface loaded phenylazoformic acid 2-phenylhydrazide was only characterized in the presence of high metal ion concentration levels.

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