



Removal and preconcentration of lead (II), copper (II), chromium (III) and iron (III) from wastewaters by surface developed alumina adsorbents with immobilized 1-nitroso-2-naphthol

Mohamed E. Mahmoud*, Maher M. Osman, Osama F. Hafez, Essam Elmelegy

Faculty of Sciences, Chemistry Department, Alexandria University, P.O. Box 426, Alexandria 21321, Egypt

ARTICLE INFO

Article history:

Received 15 May 2009

Received in revised form 18 August 2009

Accepted 19 August 2009

Available online 25 August 2009

Keywords:

Alumina
1-Nitroso-2-naphthol
Removal
Heavy metals
Wastewater

ABSTRACT

The potential removal and preconcentration of lead (II), copper (II), chromium (III) and iron (III) from wastewaters were investigated and explored. Three new alumina adsorbents of acidic, neutral and basic nature (I–III) were synthesized via physical adsorption and surface loading of 1-nitroso-2-naphthol as a possible chelating ion-exchanger. The modified alumina adsorbents are characterized by strong thermal stability as well as resistance to acidic medium leaching processes. High metal up-take was found providing this order: Cu(II) > Cr(III) > Pb(II) owing to the strong contribution of surface loaded 1-nitroso-2-naphthol. The outlined results from the distribution coefficient and separation factor evaluations (low metal ion concentration levels) were found to denote to a different selectivity order: Pb(II) > Cu(II) > Cr(III) due to the strong contribution of alumina matrix in the metal binding processes. The potential applications of alumina adsorbents for removal and preconcentration of Pb(II), Cu(II), Cr(III) from wastewaters as well as drinking tap water samples were successfully accomplished giving recovery values of $(89–100 \pm 1–3\%)$ and $(93–99 \pm 3–4\%)$, respectively without any noticeable interference of the wastewater or drinking tap water matrices.

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1. Introduction

Removal of toxic heavy metals such as lead, mercury, cadmium, chromium and arsenic from various wastewaters is considered as one of the most important and challenging areas of water treatments. The rapid and growing industrialization have led to excessive disposal of heavy metals creating major environmental pollution problems and global concern [1]. Moreover, heavy metals are often detected in wastewaters as a result of industrial activities [2]. Heavy metals are known for their non-biodegradability and accumulation in living systems, causing serious diseases and disorders.

Various methods of heavy metals removal from wastewaters have been the subject of different researches [3–6]. Most of these processes are unacceptable owing to their high cost, low efficiency, disposal of sludge, inapplicability to a wide range of pollutants [2]. Adsorption, on the other hand, is one of the most recommended physico-chemical treatment processes that is commonly used and applied for heavy metals removal from water samples and aqueous solutions. In addition, adsorption process is well recognized as one of the most efficient methods for removal of

heavy metals from their matrices. Adsorption is mainly based on the utilization of solid adsorbents from either organic, inorganic, biological or low cost materials [7,8]. Heavy metal removal via adsorption by organic adsorbents is 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 where as the target metal ions are directly attached to this kind of adsorbents via chelation or complex formation mechanism [9–12]. Naturally occurring materials, either modified or unmodified, organic adsorbents such as chitosan and crosslinked carboxymethyl-chitosan, polysaccharide-based materials and lignocellulosic fibers with their surface characteristic functional groups in the form of hydroxyl or carboxyl were also found great research interests [13–15]. Biological adsorbents, referred as biosorbents, are commonly derived from biological components such as bacteria, fungi and algae that are characterized and capable of complex formation and/or ion-exchange reactions with metal ions via their functional groups in a process known as biosorption [16,17]. Removal and extraction of heavy metals based on applications of biosorption approach are commonly performed owing to the major advantages of various biosorbents such as the economical nature, eco friendly behavior, regeneration for multiple uses and high selectivity toward different metals [2]. Low cost adsorbent materials originated from industrial products or wastes are

* Corresponding author. Tel.: +20 119112882; fax: +20 3 3911794.

E-mail address: memahmoud10@yahoo.com (M.E. Mahmoud).

also known as biosorbents and widely used for removal of heavy metals from water samples and these include components of plants, wood, grasses, compost, peat moss and carbon materials [18–24].

Inorganic solid adsorbents as alumina, silica and zirconia are well characterized by their high mechanical properties and strong resistivity to thermal degradation as compared to other biosorbents or organic adsorbents. In addition, several other advantages of alumina are characterized when used and applied as adsorbent for heavy metals removal and these include high surface area, existence in several structures and amphoteric properties [25]. Activated form of alumina is also considered as one of the most commonly used adsorbent for heavy metal removal, preconcentration and separation of trace amounts of elements in flow injection-atomic spectrometry [26]. Several reports were focused and published on the utilization of alumina types for removal of toxic heavy metals from various matrices as well as preconcentration and determination of lead in drinking waters [27]. Activated alumina can be used as both cation and anion-exchangers, depending on solution pH. Under basic conditions, alumina displays a high affinity for a wide range of cationic species [28,29] while under acidic conditions it exhibits a high affinity for anionic species [30]. Removal of Se(IV) and Se(VI) from water by alumina-coated sand was studied and reported [31]. A method was described for the immobilization of 2-mercaptopyridine on the surface of three different alumina adsorbents for preconcentration of Pb(II) and Cu(II) from sea water [32]. Alumina adsorbents–physically loaded thiosemicarbazide and thiosemicarbazone derivatives were recently reported for Cr(III)/Cr(VI) speciation in various water samples [33–35]. Heavy metal removal and binding properties of physically adsorbed 2-thiouracil on the surface of porous alumina from water samples was also described and reported [36]. Other applications of modified alumina adsorbents were also reported for removal of various toxic heavy metals from different water samples [37–39].

The present study deals with a simple, direct and efficient surface modification procedure via physical immobilization of 1-nitroso-2-naphthol, as an important analytical reagent and chelating ion-exchanger [40–42], for the formation of three modified adsorbents (I–III) based on acidic, neutral and basic alumina matrices. The feasibility of modified alumina adsorbents along with their characteristic bi-functionality based on alumina surface active groups and active donor atoms (N and O) of 1-nitroso-2-naphthol was investigated and explored in this work for removal and preconcentration of lead (II), copper (II), chromium (III) and iron (III) as well as other heavy metal ions from wastewater and drinking tap water samples by static and dynamic techniques.

2. Experimental

2.1. Chemicals and solutions

1-Nitroso-2-naphthol (formula weight = 173.17 and melting point = 106 °C) was purchased from Aldrich Chemicals and used as received. Three alumina types of standard specifications (150 mesh, 58 Å, and surface area = 155 m²/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 a 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.

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 1.0 M sodium acetate trihydrate solution by mixing the appropriate volumes of the two solutions and diluting to 1.0 l. The pH-value of resulting solutions was adjusted by a pH meter. Hydrochloric acid, sodium acetate trihydrate and 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).

2.2. Instrumentation

Thermolyne 47900 furnace was used to determine the mmol/g surface coverage values of modified alumina adsorbents via thermal desorption analysis. Infrared spectra of the modified alumina adsorbents (I–III) were recorded from KBr pellets by using a PerkinElmer spectrophotometer, model 1430. The electron impact mass spectra of blank alumina, chelating compound and modified 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. The mass spectral sheets were computerized to give I/Base and its corresponding mass. 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 by using a SHIMADZU model AA-6650.

2.3. Synthesis of alumina adsorbents–physically immobilized-1-nitroso-2-naphthol adsorbents (I–III)

A sample of 1.73 g (10.0 mmol) of 1-nitroso-2-naphthol was weighed and transferred to a 250 ml conical flask. 100 ml of toluene was then added to this sample and allowed to stir on cold until complete dissolution of the organic modifier. To this solution 10.0 ± 0.1 g of alumina, either acidic, neutral or basic type was added and the reaction mixture was further stirred for 4 h. The newly modified alumina adsorbents (I–III) were filtered, washed with 100 ml toluene on three times, 50 ml ethyl alcohol and finally with 50 ml of diethyl ether. Alumina adsorbents (I–III) were then allowed to dry in an oven adjusted to 60 °C for 8 h.

2.4. Surface coverage determination

The determination of surface coverage values of modified alumina adsorbents (I–III) were accomplished by thermal desorption method. In this method, 100 ± 1 mg of the dry alumina adsorbents (I–III) 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 min. The ignited alumina was then kept at this temperature for 1 h and left to cool down inside the furnace till 70 °C. The sample was transferred to a desiccator and left to reach to the room temperature. The weight loss of the organic chelating compound 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 alumina–physically loaded-1-nitroso-2-naphthol adsorbents (I–III).

2.5. Stability test of alumina adsorbents (I–III) in acidic solutions

A sample of modified alumina adsorbent (0.5 g) was mixed with 50 ml of the selected buffer solutions (pH 1–7) in a 100 ml volumetric flask and automatically shaken for 1 h. The mixture was filtered, washed with another 50 ml portion of the same buffer solution and DDW and dried at 70 °C. 25.0 ± 1 mg of the buffered alumina adsorbent was added to a solution containing 9.0 ml of buffer (pH 6) and 1.0 ml of 0.1 molar of Cu(II). The mixture was automatically shaken for 30 min and the degree of hydrolysis of alumina

adsorbents (I–III) in different buffer solutions was determined from the metal up-take values of Cu(II).

2.6. Determination of metal adsorption capacity

Batch equilibrium technique was used to determine the metal adsorption capacity values ($\mu\text{mol/g}$) of modified alumina adsorbents (I–III). A series of metal ions including 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 used and the metal adsorption capacity values were determined in triplicate. In this method, 50 ± 1 mg of the dry 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 a 50 ml measuring flask. These were then shaken at room temperature for 30 min by an automatic shaker. After equilibration, the mixture was filtered and washed three times with 100 ml-DDW. The unbounded metal ion was subjected to complexometric titration using 0.01M-EDTA solution or by atomic absorption spectrophotometric analysis.

Batch equilibrium technique was also used and applied to study the effect of shaking time intervals (1, 5, 10, 15, 20, 25 and 30 min) on the metal adsorption capacity and the extraction percentage of some selected metal ions according to the following procedure. A sample of 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 the optimum buffer solution. This mixture was shaken for the selected period of time, filtered, washed with 100 ml DDW and the unextracted metal ion by alumina adsorbent was determined by complexometric EDTA titration.

2.7. Determination of the distribution coefficient

Determination of the distribution coefficient values of modified alumina adsorbents (I–III) was performed by using a series of metal ions. The selected metal ions were 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 was adjusted as $\sim 1.0 \mu\text{g ml}^{-1}$ in 0.1 molar sodium acetate solution except Fe(III) was prepared in buffer pH 2. In a 25 ml measuring flask, 100 ± 1 mg of the modified alumina adsorbents (I–III) was weighed. 10 ml of $1.0 \mu\text{g ml}^{-1}$ metal ion was then added and the flask was shaken by an automatic shaker for 1 h. This mixture was filtered and washed with 10 ml DDW. The volume of metal ion was completed to 50 ml 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.

2.8. Removal and extraction of heavy metals from industrial wastewater samples by alumina adsorbents (I–III)

Wastewater samples were collected from Damnhour drug factory and spiked with ~ 1.0 – $2.0 \mu\text{g ml}^{-1}$ each of Fe(III), Cr(III), Cu(II) and Pb(II) followed by flame atomic absorption analysis of these samples. The extraction procedure of these heavy metal ions from water samples was accomplished by running 1.0 l over a micro-column packed with 500 mg of the selected modified alumina adsorbent with a flow rate 10.0 ml min^{-1} . The effluent solution was collected and acidified with hydrochloric acid and subjected for atomic absorption spectrophotometric analysis of the unextracted metal ion. Wastewater samples were also subjected for atomic absorption spectrophotometric analysis before running over the micro-column. A blank sample was also measured by atomic absorption spectrophotometric analysis for the direct comparison.

Table 1

Surface coverage and pH-values of alumina adsorbents–physically adsorbed 1-nitroso-2-naphthol (I–III).

Alumina phase	pH-value	Thermal desorption (mmol/g)	Metal probe (mmol/g)
Blank acidic alumina	4.4	–	–
Blank neutral alumina	6.7	–	–
Blank basic alumina	8.9	–	–
Modified acidic alumina (I)	4.3	0.352	0.440
Modified neutral alumina (II)	5.4	0.349	0.450
Modified basic alumina (III)	6.0	0.345	0.450

Values of mmol/g are the average of triplicate determination with %RSD = 1–3.

2.9. Preconcentration of heavy metals from drinking tap water

Preconcentration of Cr(III), Fe(III) and Pb(II) was performed according to this procedure. 1.0 l of drinking tap water sample was spiked with $\sim 5.0 \text{ ng ml}^{-1}$ of the target metal ion. Water samples were then passed over a preconcentration micro-column packed with 500 mg-modified alumina adsorbents (I–III) with a flow rate of ($\sim 10.0 \text{ ml min}^{-1}$) 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.

3. Results and discussion

3.1. Surface coverage and characterization

Determination of the surface coverage values of modified alumina adsorbents can be accomplished by several well known methods including thermal desorption method as well as metal probe testing method [32–34]. The surface coverage values of the newly modified alumina–physically adsorbed 1-nitroso-2-naphthol adsorbents (I–III) were determined by these two previously mentioned methods. The determined surface coverage values based on this method were found to be 0.352, 0.349 and 0.345 mmol/g for modified alumina adsorbent–physically adsorbed 1-nitroso-2-naphthol (I), (II) and (III), respectively. These values confirm the possible binding via adsorption of 1-nitroso-2-naphthol on the surface of either an acidic, neutral or basic alumina type. The closeness in the mmol/g surface coverage values for these modified alumina adsorbents (I–III) proves that there is no role for the pH-values of the blank unmodified acidic, neutral and basic alumina adsorbents in the physical adsorption process. The reason for such similar behavior and trends of newly modified alumina adsorbents (I–III) is mainly due to the close pH range (4.3–6.0) of these adsorbents as listed in Table 1. The second method used in this work for determination of the surface coverage values is the metal probe testing. In this method, the highest bound metal to the surface of newly modified adsorbent, as determined and evaluated by the metal sorption capacity $\mu\text{mol/g}$ value, is usually taken as a representative value for the surface coverage of this modified adsorbent. According to this method, the estimated surface coverage mmol/g value for modified acidic alumina adsorbent (I) was found to be 0.440 mmol/g based on the value of metal sorption capacity of Cu(II). The modified neutral and basic alumina adsorbents–physically adsorbed 1-nitroso-2-naphthol (II) and (III) were found to be 0.450 mmol/g as identified from the metal capacity values of Cu(II) with these two alumina adsorbents. The reason for such high surface coverage determination by this method may be attributed to the contribution of the alumina matrix owing to the ion-exchange characters incorporated into these types of

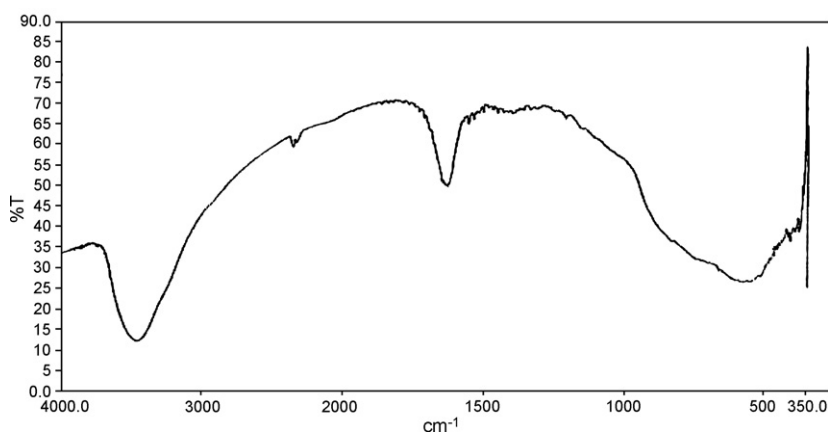


Fig. 1. Infrared spectrum of alumina adsorbent (III).

solid supports [43,44]. Table 1 compiles the surface coverage values of newly modified alumina adsorbents—physically adsorbed 1-nitroso-2-naphthol (I–III) as determined by the thermal desorption and metal probe-testing methods. The pH-values of blank unmodified alumina and modified alumina adsorbents (I–III) are also listed.

Surface modification of solid supports, as alumina, with organic modifiers, as chelating compounds, can be generally characterized on the basis of determination and analysis of the newly modified alumina adsorbents (I–III) by infrared spectrophotometric method. The infrared spectrum of 1-nitroso-2-naphthol exhibited several characteristic infrared peaks at 3450, 3150, 1550, (1638, 1581, 1450) cm^{-1} due to ν -OH, ν -CH aromatic, ν -NO and ν -C=C, respectively. The blank acidic, neutral and basic alumina adsorbents showed the characteristic peaks at 3600–3400, 1650 and 1000–400 cm^{-1} that are mainly due to the alumina matrix [32]. However, the IR-spectra of modified alumina adsorbents (I–III) are dominated by the peaks corresponding to the alumina matrix as shown in Fig. 1 and provided as a representative example. The characteristic peaks of surface loaded 1-nitroso-2-naphthol were identified as weak or very weak ones owing to the determined low surface coverage or percentage of this organic modifier.

3.2. Stability of the alumina adsorbents

3.2.1. Thermal stability

Mass spectrometry technique is one of the powerful analytical methods of analysis for qualitative and quantitative determination of organic and inorganic compounds. It can be used for the identification of products formation as well as study of surface modification and thermal decomposition of loaded organic compounds [45]. Thus, alumina adsorbents—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 to 300–350 °C in a way similar to that described and known for pyrolysis of polymer compounds by mass spectrometric technique [46]. The mass spectra of 1-nitroso-2-naphthol and blank acidic, neutral and basic alumina matrices were studied for the sake of comparison with newly modified alumina adsorbents (I–III). The 70-eV EI-MS-DIP of 1-nitroso-2-naphthol as an organic modifier was characterized by the presence of the base peak at m/z 173 (100%) as the molecular ion. In addition, two other fragment ions at m/z 156 (46%) and 143 (12%) and these two peaks are related to the loss of the hydroxyl and nitroso group from the molecular

ion, respectively. Some other fragment ion peaks at 127 (27%), 115 (25%), 101 (7%), 89 (5%), 76 (3%) and 51 (3%) are related and derived from the ionization of the naphthalene ring moiety. The 70-eV EI-MS-DIP of blank acidic alumina exhibited a peak at m/z 18 which is mainly due to the presence of either adsorbed water molecules on the surface of blank acidic alumina adsorbent 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 spectral peak at m/z 44 which corresponds to the presence of CO_2 molecule [47]. No other characteristic fragment ion peaks could be identified from the mass spectrum of blank alumina. The 70-eV EI-MS-DIP spectrum of modified acidic alumina adsorbent (I) showed also the characteristic three masses at 18, 28 and 44 which are related to H_2O , N_2 and CO_2 molecules respectively. No evidence for the molecular ion at m/z 173, but only few low abundant (<2%) fragment ions, that are related to the organic modifier, at m/z 143, 127, 105 and 83 and these can be directly refer to the surface modification of acidic alumina with 1-nitroso-2-naphthol. In addition, one can easily conclude that modified acidic alumina adsorbent (I) is highly thermally stable under the studied heating temperature range.

The same trend and observation were identified and characterized in the 70-eV EI-MS-DIP spectra of modified alumina adsorbents (II) and (III).

3.2.2. Medium stability

The stability of modified alumina adsorbents—physically adsorbed 1-nitroso-2-naphthol (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, 1-nitroso-2-naphthol, from the surface of each alumina adsorbent. The results of this study proved that modified alumina adsorbent (I) is highly stable in most buffer solutions (pH 2–6) with a percentage stability of 91%. Only solution with pH 1.0 was found to exhibit high leaching or hydrolysis (<83% stability) of the organic modifier from the adsorbent surface. Modified neutral alumina adsorbent—physically adsorbed 1-nitroso-2-naphthol (II) was found to be highly stable in buffer solutions (pH 3–5) with a percentage stability of >89% while in the other pH solutions as pH 1 and 2, the percent stability values were found to be less than 80.0%. Newly modified basic alumina adsorbent (III) was found to be highly stable in buffer solutions pH 3–7 with a stability value (>90%) at pH 6.0 and high leaching processes were detected in lower pH solutions. Thus, it is evident that the stability of these modified alumina adsorbents (I–III) are highly identified in the working pH range 3–6.

Table 2
Metal adsorption capacity ($\mu\text{mol/g}$) in optimum pH.

Metal ion	Phase (I)		Phase (II)		Phase (III)	
	$\mu\text{mol/g}$	pH	$\mu\text{mol/g}$	pH	$\mu\text{mol/g}$	pH
Mg(II)	00	1–7	00	1–7	00	1–7
Ca(II)	00	1–7	10	1–7	00	1–7
Cr(III)	240–270	6–7	240	6–7	240	6–7
Mn(II)	00	1–7	00	1–7	00	1–7
Fe(III)	100	3–4	100	3–4	80–100	3–4
Co(II)	10	6	00	1–7	00	1–7
Ni(II)	20–30	6–7	20–30	6–7	20–30	6–7
Cu(II)	440	7	450	7	450	7
Zn(II)	20–30	6–7	20–40	6–7	40	7
Cd(II)	10	6–7	00	4–7	00	4–7
Hg(II)	100	6–7	60–100	6–7	60–100	6–7
Pb(II)	180	7	180	7	190	7

Values of $\mu\text{mol/g}$ are the average of triplicate analysis with %RSD = 0–2.

3.3. Metal adsorption properties of modified alumina adsorbents (I–III)

3.3.1. Effect of pH-value on the metal adsorption capacity

The effect of pH of tested metal ion solutions on the amount extracted by the modified alumina adsorbent 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 1-nitroso-2-naphthol at certain pH-values. Metal capacity values (MC_t) at any time, expressed in $\mu\text{mol/g}$, can be calculated based on Eq. (1).

$$MC_t = \frac{(C_0 - C_t)V_{ml}}{\text{Mass}_g} \times 1000 \quad (1)$$

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. Table 2 summarizes the determined metal adsorption capacity values, expressed in $\mu\text{mol/g}$, for the tested metal ions along with the optimum pH for binding of each metal ion.

It is evident from the listed metal adsorption capacity values that the pH range 6–7 is the optimum ones for forcing maximum binding and extraction processes between newly modified alumina adsorbents (I–III) with most metal ions as Cr(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pb(II) and Hg(II). On the other hand, Mg(II), Ca(II) and Mn(II) were found to show no or little tendency to bind and extract by any one of the modified alumina adsorbents judging from the determined metal adsorption capacity values (0–10 $\mu\text{mol/g}$). The pH-value of contact solution of metal ion and alumina adsorbent was also found to show no effect in binding and extraction process of Mg(II), Ca(II) and Mn(II) by modified alumina adsorbents (I–III). Fe(III) was found to give its maximum metal capacity (80–100 $\mu\text{mol/g}$) by the three modified alumina adsorbents (I–III) in the pH range 3–4. However, Fe(III) was only examined in solutions of pH 1–4 to avoid any precipitation of $\text{Fe}(\text{OH})_3$ in presence of buffer solutions with pH 5–7.

In addition, it is also evident from the data of metal adsorption capacity values listed in Table 2 that most of the tested metal ions were found to exhibit similar binding properties with the three newly modified alumina adsorbents (I–III). For example, the metal adsorption capacity values of Ni(II) were found to be the same (20–30 $\mu\text{mol/g}$) for alumina adsorbents (I), (II) and (III). Cu(II) was found as the highest extracted metal ion giving rise to metal adsorption capacity values of 440, 450 and 450 $\mu\text{mol/g}$ for modified alumina adsorbents (I), (II) and (III), respectively. Hg(II) behaved in a similar fashion as other metal ions giving metal adsorption capacity values of 100, 60–100 and 60–100 $\mu\text{mol/g}$ for modified alumina adsorbents (I), (II) and (III), respectively. However, it is important to

compare the identified metal adsorption capacity values of modified alumina adsorbents (I–III) with those determined for the same metal ions by blank acidic, neutral and basic alumina adsorbents. The blank adsorbents were found to exhibit similar trends of metal up-take capacity values ($\leq 10 \mu\text{mol/g}$) for Mg(II), Ca(II) and Mn(II) in all buffer solutions. However, blank acidic, neutral and basic alumina adsorbents were characterized by their low affinity for other tested metal ions such as Cr(III), Cu(II), Pb(II) or Hg(II) compared to modified alumina adsorbents (I–III). The determined metal adsorption capacity values by blank alumina adsorbents were found in the range of 40–60, 70–100, 10–20 and 20–30 $\mu\text{mol/g}$ for Cr(III), Cu(II), Pb(II) and Hg(II), respectively. Thus, one can conclude from the results and discussion of metal adsorption properties of alumina adsorbents (I–III) that the organic modifier, 1-nitroso-2-naphthol is the major directing and acting force in the processes of metal up-take and adsorption by modified alumina adsorbents (I–III). In addition, acidic-basic characters of blank alumina adsorbents has no role in directing the metal capacity toward either one and this conclusions proves the suitability and equal efficiency of any modified alumina adsorbent either, acidic or neutral or basic for use and application in metal ion extraction and separation. However, the adsorption properties of blank acidic, neutral and basic alumina adsorbents toward various metal ions were extensively studied, explored and evaluated in our previously published work [32] and the results can be clearly used to show a direct comparison with modified alumina adsorbents. This conclusion can also be confirmed from the following close increasing orders for the tested metal ions by the newly modified alumina adsorbents (I–III).

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

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

3.3.2. Effect of shaking time on the metal adsorption capacity

The importance of shaking time comes from the need for identification of the possible rapidness of binding and extraction processes of the tested metal ions by the newly modified adsorbents. 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 adsorbents or chelating polymers as well as the optimum time is usually useful when separation of metal ions from each other is aimed. For these reasons only two metal ions were selected to conduct this study and these are Cu(II) and Pb(II).

Figs. 2 and 3 represent the effect of selected shaking time values (1, 5, 10, 15, 20, 25 and 30 min) on the percentage extraction of the tested metal ions. It is clear from Fig. 2 that Cu(II) was similarly behaving toward extraction by the three newly modified alumina adsorbents (I–III). Very close percentage extraction values can be observed under the identical shaking time values. In addition, Cu(II) was found to show percentage extraction values of ~80% when only 5-min shaking time was used. This time shows also that fast equilibration of Cu(II) with either alumina adsorbent (I) or (II) or (III). There is no superiority evidence of any adsorbent in the extraction process of Cu(II), but only similar trends and behaviors as previously described in Section 3.3.1.

The same trends, observations, arguments and conclusions can be outlined for the extraction of Pb(II) by modified alumina adsorbents (I–III) as shown in Fig. 3. It is evident from Fig. 2 that Pb(II) was found to behave in a close fashion toward extraction by the three modified alumina adsorbents (I–III). Moreover, under identi-

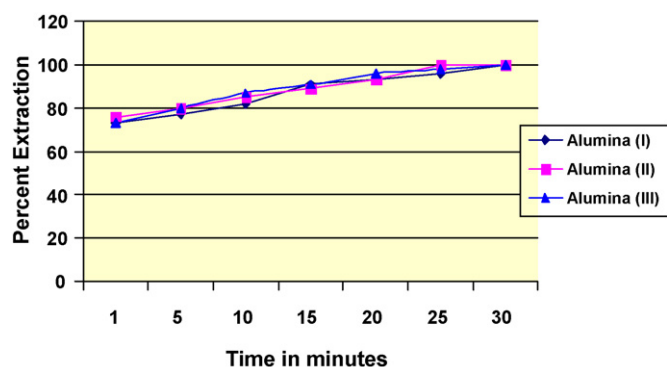


Fig. 2. Effect of shaking time on the percent extraction of Cu(II) by modified alumina adsorbents (I–III).

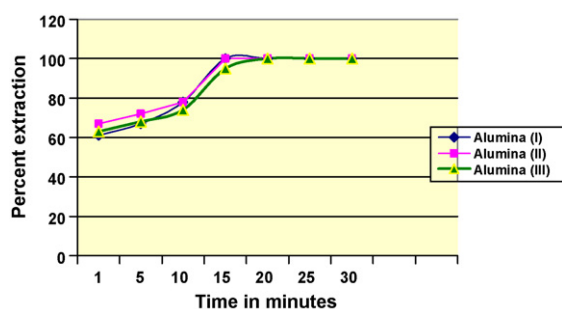


Fig. 3. Effect of shaking time on the percent extraction of Pb(II) by modified alumina adsorbents (I–III).

cal shaking time values, very close percentage extraction trends of Pb (II) were observed. However, the only basic difference between extraction of Pb(II) versus Cu(II) is the somewhat slowness of Pb(II) extraction by the three modified alumina adsorbents (I–III). More than 10-min of shaking time were needed to reach a range of 80% extraction of Pb (II) by alumina adsorbents (I–III). However, complete extraction of Pb(II) by alumina adsorbents (I–III) was reached after 15-min of shaking time.

3.4. Distribution coefficients and separation factors

Evaluation of the metal binding properties is considered more convenient by the distribution coefficient (K_d) when the possible concentrations of the tested metal ions are in very low concentration levels especially in the range of part per million or part per billion. The K_d -value is determined from Eq. (2).

$$K_d = \frac{\text{mmol of extracted metal ion/g-alumina phase}}{\text{mmol of unextracted metal ion/volume of solution}} \quad (2)$$

The separation factor 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 calculated from the distribution coefficient values K_d (A) and K_d (B), respectively as given in Eq. (3).

$$\alpha_{A/B} = \frac{K_d(A)}{K_d(B)} \quad (3)$$

The distribution coefficient values of various tested metal ions as determined by modified alumina adsorbents (I–III) are given in Table 3. It is evident from Table 3 that Fe(III) is the highest extracted ion by modified acidic alumina adsorbent (I) with a $K_d = 902$. Pb(II) was found to be give a $K_d = 631$ as the second highest extracted metal ion by modified alumina adsorbent (I). This conclusion can be confirmed by evaluation of the separation factors for these tested

Table 3
Distribution coefficient of metal ions.

Metal ion	Adsorbent (I)	Adsorbent (II)	Adsorbent (III)
Mg(II)	10	80	100
Ca(II)	63	501	631
Cr(III)	59	3162	6940
Mn(II)	42	631	1000
Fe(III)	902	2512	1585
Co(II)	130	1000	1000
Ni(II)	153	1259	1995
Cu(II)	63	7943	7943
Zn(II)	40	794	1589
Cd(II)	30	1000	1589
Pb(II)	631	50119	39811

Distribution coefficient values are the average of triplicate analysis with %RSD = 0–3.

metal ions. The separation factor $\alpha_{A/B}$ for Fe(III) versus other tested metal ions by modified acidic alumina adsorbent (I) were also determined and evaluated. It is evident that Fe(III) can be selectively extracted from other interfering metal ions as Mg(II), Cd(II), Zn(II), Cr(III), Mn(II), Cu(II), Ca(II). Possible interference of some metal ions as Co(II), Ni(II) and Pb(II) due to the low calculated separation factors for Fe(III) versus these three metal ions.

Table 3 compiles also the data of distribution coefficient values for the tested metal ions as determined by the modified neutral alumina adsorbent (II). Fig. 4 represents the separation factors calculated of Pb(II) versus other interfering metal ions. It is evident from the data in both Table 3 and Fig. 4 that physical adsorption and binding of 1-nitroso-2-naphthol on the surface of neutral alumina phase (II) has forced some selective characters in binding with certain metal ions as Pb(II), Cu(II) and Cr(III). It is also evident from Fig. 4 that Pb(II) can be selectively removed and separated from other interfering metal ions as Mg(II) ($\alpha_{Pb/Mg} = 626.5$), Ca(II) ($\alpha_{Pb/Ca} = 100.0$), Mn(II) ($\alpha_{Pb/Mn} = 79.4$), Cr(III) ($\alpha_{Pb/Cr} = 15.9$), Fe(III) ($\alpha_{Pb/Fe} = 20.0$), Co(II) ($\alpha_{Pb/Co} = 50.1$), Ni(II) ($\alpha_{Pb/Ni} = 39.8$), Zn(II) ($\alpha_{Pb/Zn} = 63.1$), Cd(II) ($\alpha_{Pb/Cd} = 50.1$) and ($\alpha_{Pb/Cu} = 6.3$). No possible interference in the process of selective removal of Pb(II) is expected owing to the high separation factor values of lead versus these interfering metal ions.

The values of the distribution coefficient for the tested metal ions by modified basic alumina adsorbent (III) are listed in Table 3. Fig. 5 shows the separation factors of Pb(II) versus other interfering metal ions. In the same manner, modified basic alumina adsorbent (III) was also found to exhibit certain selectivity properties toward Pb(II), Cu(II) and Cr(III). Possible selective separation of Pb(II) from Mg(II), Ca(II), Mn(II), Fe(III), Co(II), Ni(II), Zn(II) and Cd(II) due to high separation factors as evident from Fig. 5. In addition, no possible interference of both Cu(II) and Cr(III) in the selective separation of Pb(II) by the newly modified basic alumina phase (III).

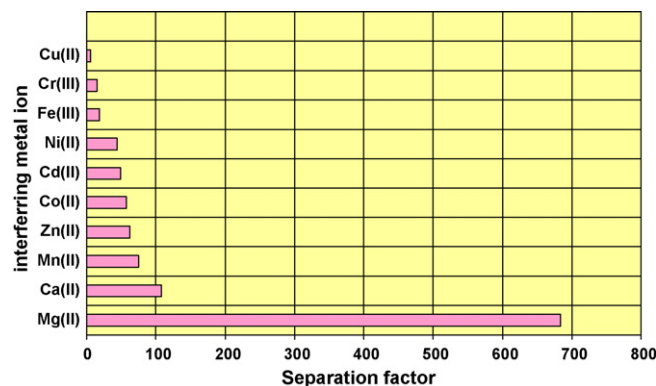


Fig. 4. Separation factors of Pb(II) versus other interfering metal ions by alumina adsorbent (II).

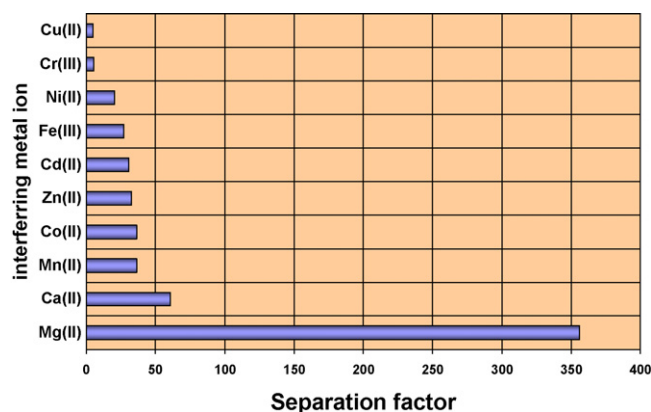


Fig. 5. Separation factors of Pb(II) versus other interfering metal ions by alumina adsorbent (III).

Comparison of the results obtained by determination of metal capacity versus distribution coefficient refers to the following points. Considering the results of metal adsorption capacity study, one can easily conclude that first, the three studied modified alumina adsorbents (I–III) are similar in their metal up-take and adsorption properties ($\text{Cu(II)} > \text{Cr(III)} > \text{Pb(II)}$) when the concentration levels of metal ions are high in the mol l^{-1} or mmol l^{-1} range. Second, the same orders of affinity and selectivity toward various tested metal ions were elucidated regardless of the mmol/g adsorption capacity values. Third, the effect of pH-values of the newly synthesized alumina adsorbents (I–III), given in Table 1, is showing no significant difference between these adsorbents. Fourth, the surface loaded 1-nitroso-2-naphthol 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 the distribution coefficient determination, the following points are apparent. First, neutral and basic alumina adsorbents are similarly behaving toward various tested metal ions ($\text{Pb(II)} > \text{Cu(II)} > \text{Cr(III)}$), while acidic alumina adsorbent (I) was differently behaving giving this order $\text{Fe(III)} > \text{Pb(II)}$. The high affinity of adsorbent (I) for Fe(III) is strongly assisted by the pH of the acidic alumina as well as soft–hard acid–base phenomenon. Second, the order of the distribution coefficient values increases from acidic alumina (I) to neutral alumina (II) to 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 modified alumina matrix. Third, 1-nitroso-2-naphthol 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 acidic, neutral or basic. Thus, the conclusion that can be drawn from this comparative study refers to the necessity of performing both studies, distribution coefficient and metal adsorption capacity, for accurate and practical evaluation of the affinity and selectivity characters incorporated into modified alumina adsorbents for removal of toxic heavy metals.

Table 5
Preconcentration of heavy metals from drinking tap water by modified alumina adsorbents (I–III).

Alumina adsorbent	Sample volume (l)	Metal ion	ng ml^{-1} Spiked	$\mu\text{g ml}^{-1}$ Detected	Percent extraction
500 mg (I)	1.0	Fe(III)	5.097	0.950	$93 \pm 3\%$
500 mg (II)	1.0	Pb(II)	5.280	1.050	$99 \pm 4\%$
500 mg (III)	1.0	Cr(III)	5.160	0.980	$95 \pm 3\%$

Values are based on triplicate analysis with %RSD = 3–4.

Table 4
Removal of toxic heavy metals from wastewaters by modified alumina adsorbents (I–III).

Alumina phase	Metal ion	mg l^{-1} Spiked	mg^{-1} Detected	Percent extraction*
500 mg (I)	Pb(II)	1.517	0.136	$91 \pm 3\%$
	Fe(III)	1.699	0.200	$89 \pm 3\%$
500 mg (II)	Cu(II)	1.471	0.002	$99 \pm 1\%$
	Pb(II)	2.034	0.001	$100 \pm 1\%$
500 mg(III)	Cr(III)	1.344	0.108	$92 \pm 2\%$
	Cu(II)	1.427	0.041	$97 \pm 2\%$
	Pb(II)	1.503	0.080	$94 \pm 2\%$

* Values are based on triplicate analysis with %RSD = 1–3.

3.5. Removal and preconcentration of Cr(III), Fe(III), Cu(II) and Pb(II) from water samples by modified alumina adsorbents (I–III)

Toxic heavy metals such as chromium, copper, mercury, cadmium and lead are excessively released into the environments due to rapid industrialization and are often detected in untreated industrial wastewaters, which originate from various industrial activities. Removal of these toxic species from industrial wastewaters by adsorption 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 Cr(III), Fe(III), Cu(II) and Pb(II) from wastewater samples collected from drug factory.

Table 4 summarizes the results of metal removal and extraction by modified alumina adsorbents (I–III) via micro-column application. It is evident from the values given in Table 4 that modified alumina adsorbents (II) and (III) are superior in the processes of removal of heavy metal ions from wastewater samples. Modified alumina adsorbent (III) was found to give percentage recovery values of 92–97% for the spiked concentration of Cr(III), Cu(II) and Pb(II). Modified alumina adsorbent (II) was found to give an excellent percentage recovery value for the spiked concentration of Cu(II) and Pb(II). Modified alumina adsorbent (I) was found to show 91% and 89% percentage recovery values of the spiked concentration of Pb(II) and Fe(III), respectively as listed in Table 4. One can easily identify that the three modified alumina adsorbents are experienced with excellent recovery values for removal of the examined heavy metal ions without possible interference of the matrix effect caused by the dissolved organic and inorganic components in the wastewater samples.

Atomic absorption spectrophotometry (AAS) has been widely used for the determination of metal ions via application of selective extraction and preconcentration techniques as the direct and possible solution to remove co-existing species that interfere in the detection process as well as to lower the detection limits of AAS. The preconcentration technique, also known as enrichment, is usually used to increase analyte/matrix ratio.

Metal preconcentration procedure was used in this section to extract and preconcentrate $\sim 5.000 \text{ ng ml}^{-1}$ of Fe(III), Pb(II) and Cr(III) from drinking tap water samples by modified alumina adsorbents (I), (II) and (III), respectively via micro-column application. Table 5 summarizes the results of this preconcentration step by using 5 ml concentrated HNO_3 as a preconcentration

reagent for satisfying a preconcentration factor of 200. One can conclude that an excellent percentage recovery value ($99 \pm 4\%$) was established for preconcentration of Pb(II) by modified neutral alumina adsorbent (II). The recovery of the spiked concentration of Cr(III) (5.160 ng ml^{-1}) was found to give a percentage recovery value equal $95 \pm 3\%$ by the application of modified alumina adsorbent (III). Finally, preconcentration of Fe(III) by modified acidic alumina adsorbent was found to give $93 \pm 3\%$ of the spiked concentration.

4. Conclusion

The present study proves the capability and effectiveness of newly modified alumina–physically immobilized-1-nitroso-2-naphthol adsorbents (I–III) for heavy metals removal from various water samples. Modified alumina adsorbents were characterized by strong stability toward acid leaching and thermal decomposition. When high concentration levels of interacting metals are used, the modified alumina adsorbents are characterized by excellent similarity in their metal binding orders and by showing almost identical behaviors owing to the strong contribution of the surface loaded 1-nitroso-2-naphthol. The participation of 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. Removal and preconcentration of heavy metals from wastewater and drinking tap water by modified alumina adsorbents were successfully accomplished without any matrix effects caused by the interference of co-existing organic or inorganic species.

References

- [1] Z. Li, X. Chang, Z. Hu, X. Huang, X. Zou, Q. Wu, R. Nie, Zincon-modified activated carbon for solid-phase extraction and preconcentration of trace lead and chromium from environmental samples, *J. Hazard. Mater.* 166 (2009) 133–137.
- [2] C. Quintelas, Z. Rocha, B. Silva, B. Fonseca, H. Figueiredo, T. Tavares, Removal of Cd(II), Cr(VI), Fe(III) and Ni(II) from aqueous solutions by an *E. coli* biofilm supported on kaolin, *Chem. Eng. J.* 149 (2009) 319–324.
- [3] C.O. Ijagbemi, M.-H. Baek, D.-S. Kim, Montmorillonite surface properties and sorption characteristics for heavy metal removal from aqueous solutions, *J. Hazard. Mater.* 166 (2009) 538–546.
- [4] A.K. Bhattacharya, S.N. Mandal, S.K. Das, Adsorption of Zn (II) from aqueous solution by using different adsorbents, *Chem. Eng. J.* 123 (2006) 43–51.
- [5] F. Pagnanelli, S. Mainelli, L. Bornoroni, D. Dionisi, L. Toro, Mechanisms of heavy-metal removal by activated sludge, *Chemosphere* 75 (2009) 1028–1034.
- [6] R. Han, L. Zou, X. Zhao, Y. Xu, F. Xu, Y. Li, Y. Wang, Characterization and properties of iron oxide-coated zeolite as adsorbent for removal of copper(II) from solution in fixed bed column, *Chem. Eng. J.* 149 (2009) 123–131.
- [7] V. Camel, Solid phase extraction of trace elements, *Spectrochim. Acta Part B* 58 (2003) 1177–1233.
- [8] P.K. Jai, S. Patel, B.K. Mishra, Chemical modification of silica surface by immobilization of functional groups for extractive concentration of metal ions, *Talanta* 62 (2004) 1005–1028.
- [9] M.E. Mahmoud, E.M. Soliman, A. El-Dissouky, Metal up-take properties of polystyrene resin-immobilized-polyamine and formylsalicylic acid derivatives as chelation ion exchangers, *Anal. Sci.* 13 (1997) 765–769.
- [10] F. Gode, E. Pehlivan, A comparative study of two chelating ion-exchange resins for the removal of chromium(III) from aqueous solution, *J. Hazard. Mater.* 100 (2003) 231–243.
- [11] J.L. Cortina, N. Miralles, Kinetic studies on heavy metals ions removed by impregnated resins containing di-(2,4,4-trimethylpentyl) phosphinic acid, *Solv. Extr. Ion Exch.* 15 (1997) 1067–1083.
- [12] R.N. Mendoza, T.I.S. Medina, A. Vera, M.A. Rodriguez, E. Guibal, Study of the sorption of Cr(III) with XAD-2 resin impregnated with di-(2,4,4-trimethyl phenyl) phosphinic acid (CYANE-X272), *Solv. Extr. Ion Exch.* 18 (2000) 319–343.
- [13] S. Sun, A. Wang, Adsorption properties of carboxymethyl-chitosan and crosslinked carboxymethyl-chitosan resin with Cu(II) as template, *Sep. Purif. Technol.* 49 (2006) 197–204.
- [14] G. Crini, Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment, *Prog. Polym. Sci.* 30 (2005) 38–70.
- [15] B.G. Lee, R.M. Rowell, Removal of heavy metal ions from aqueous solutions using lignocellulosic fibers, *J. Nat. Fibers* 1 (2004) 97–108.
- [16] B. Volesky, *Biosorption and me*, *Water Res.* 41 (2007) 4017–4029.
- [17] M.E. Mahmoud, A.A. Yakout, M.M. Osman, Dowex anion exchanger-loaded-Baker's yeast as bi-functionalized biosorbents for selective extraction of anionic and cationic mercury(II) species, *J. Hazard. Mater.* 164 (2009) 1036–1044.
- [18] J. Romero-Gonzalez, J.R. Peralta-Videa, E. Rodriguez, M. Delgado, J.L. Gardea-Torresdey, Potential of *Agave lechuguilla* biomass for Cr(III) removal from aqueous solutions: thermodynamic studies, *Bioresour. Technol.* 97 (2006) 178–182.
- [19] M.F. Sawalha, J.L. Gardea-Torresdey, J.G. Parsons, G. Saupe, J.R. Peralta-Videa, Determination of adsorption and speciation of chromium species by salt-bush (*Atriplex canescens*) biomass using a combination of XAS and ICP-OES, *Microchem. J.* 81 (1) (2005) 122–132.
- [20] D.C. Sharma, C.F. Forster, Column studies into the adsorption of chromium(VI) using sphagnum moss peat, *Bioresour. Technol.* 52 (1995) 261–267.
- [21] S.D.C. Sharma, C.F. Forster, Continuous adsorption and desorption of chromium ions by sphagnum moss peat, *Proc. Biochem.* 30 (1995) 293–298.
- [22] G. Carrillo-Morales, M.M. Davila-Jimenez, M.P. Elizalde-Gonzalez, A.A. Pelaez-Cid, Removal of metal ions from aqueous solution by adsorption on the natural adsorbent CACMM2, *J. Chromatogr. A* 938 (2001) 237–242.
- [23] D. Mohan, C.U. Pittman Jr., Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water, *J. Hazard. Mater.* B137 (2006) 762–811.
- [24] L. Monser, N. Adhoum, Modified activated carbon for the removal of copper, zinc, chromium and cyanide from wastewater, *Sep. Purif. Technol.* 26 (2002) 137–146.
- [25] T.K. Naiya, A.K. Bhattacharya, S.K. Das, Adsorption of Cd(II) and Pb(II) from aqueous solutions on activated alumina, *J. Colloid Interf. Sci.* 333 (2009) 14–26.
- [26] C.W. McLeod, Flow injection techniques in inductively coupled plasma spectrometry. Plenary lecture, *J. Anal. At. Spectrom.* 2 (1987) 549–552.
- [27] Y. Zhang, P. Riby, A.G. Cox, C.W. McLeod, A.R. Date, Y.Y. Cheung, On-line preconcentration and determination of lead in potable water by flow injection atomic absorption spectrometry, *Analyst* 113 (1988) 125–128.
- [28] A.G. Cox, C.W. McLeod, Preconcentration and determination of trace chromium(III) by flow injection/inductively-coupled plasma/atomic emission spectrometry, *Anal. Chim. Acta* 179 (1986) 487–490.
- [29] K. Yamada, C.W. McLeod, O. Kujirai, H. Okachi, On-line enrichment and determination of trace sulfur in high-purity iron samples by flow injection and inductively coupled plasma atomic emission spectrometry, *J. Anal. At. Spectrom.* 7 (1992) 661–1661.
- [30] S. Dadfarnia, M.H. Jafarzadeh, Online trace enrichment and determination of cobalt ion as an anionic complex by flow injection atomic absorption spectrometry, *Microchem. J.* 63 (1999) 226–234.
- [31] W.H. Kuan, S.L. Lo, M.K. Wang, C.F. Lin, Removal of Se(IV) and Se(VI) from water by aluminum-oxide-coated sand, *Water Res.* 32 (1998) 915–923.
- [32] M.E. Mahmoud, Study of the selectivity characteristics incorporated into physically adsorbed alumina phases-2-mercaptocotinic acid and potential applications as selective stationary phases for separation, extraction and preconcentration of lead (II) and copper (II), *J. Liq. Chrom. Rel. Technol.* 25 (2002) 1187–1199.
- [33] M.E. Mahmoud, A.A. Yakout, S.B. Ahmed, M.M. Osman, Speciation, selective extraction and preconcentration of chromium ions via alumina-functionalized-isatin-thiosemicarbazone, *J. Hazard. Mater.* 158 (2008) 541–548.
- [34] M.E. Mahmoud, A.A. Yakout, S.B. Ahmed, M.M. Osman, Development of a method for chromium speciation by selective solid phase extraction and preconcentration on alumina-functionalized-thiosemicarbazide, *J. Liq. Chromatogr. Rel. Technol.* 31 (2008) 2475–2492.
- [35] M.E. Mahmoud, A.A. Yakout, S.B. Ahmed, M.M. Osman, Chromium speciation, selective extraction and preconcentration by alumina-functionalized-2-pyridenecarboxaldehyde thiosemicarbazone, *Int. J. Environ. Anal. Chem.* 88 (2008) 1017–1031.
- [36] M.E. Mahmoud, M.S. Massoud, N.N. Maximov, Synthesis, characterization, and selective metal binding properties of physically adsorbed 2-thiouracil on the surface of porous silica and alumina, *Mikrochim. Acta* 147 (2004) 111–115.
- [37] E.M. Soliman, M.B. Saleh, S.A. Ahmed, Alumina modified by dimethyl sulfoxide as a new selective solid phase extractor for separation and preconcentration of inorganic mercury(II), *Talanta* 69 (2006) 55–60.
- [38] X. Pu, Z. Jiang, B. Hu, H. Wang, γ -MPTMS modified nanometer-sized alumina micro-column separation and preconcentration of trace amounts of Hg, Cu, Au and Pd in biological, environmental and geological samples and their determination by inductively coupled plasma mass spectrometry, *J. Anal. At. Spectrom.* 19 (2004) 984–994.
- [39] G. Absalan, M.A. Mehrdardi, Separation and preconcentration of silver ion using 2-mercaptobenzothiazole immobilized on surfactant-coated alumina, *Sep. Purif. Technol.* 33 (2003) 95–101.
- [40] V. Chand, S. Prasad, Trace determination and chemical speciation of selenium in environmental water samples using catalytic kinetic spectrophotometric method, *J. Hazard. Mater.* 165 (2009) 780–788.
- [41] M. Pesavento, G. Alberti, R. Biesuz, Analytical methods for determination of free metal ion concentration, labile species fraction and metal complexation capacity of environmental waters: a review, *Anal. Chim. Acta* 631 (2009) 129–141.
- [42] S.Q. Memon, M.I. Bhangar, S.M. Hasany, M.Y. Khuhawar, The efficacy of nitrosonaphthol functionalized XAD-16 resin for the preconcentration/sorption of Ni(II) and Cu(II) ions, *Talanta* 72 (2007) 1738–1745.
- [43] K.K. Unger, *Packing and Stationary Phases in Chromatographic Techniques*, Marcel Dekker, New York, 1990.

- [44] H.A. Mottola, J.R. Steimetz, *Chemically Modified Surfaces*, Elsevier, New York, 1992.
- [45] M.E. Mahmoud, S.S. Haggag, T.M. Abdel-Fattah, Synthesis, characterization and metal chelating properties of silica-physisorbed and chemisorbed-2,5-dioxypiperazine, *Polyhedron* 26 (2007) 3956–3962.
- [46] M.E. Mahmoud, S.S. Haggag, A.H. Hegazi, Synthesis, characterization and sorption properties of silica gel-immobilized-pyrimidine derivative, *J. Colloid Interf. Sci* 300 (2006) 94–99.
- [47] M.E. Mahmoud, M.M. El-Essawi, S.A. Kholeif, E.I. Fathallah, Aspects of surface modification, structure characterization, thermal stability and metal selectivity properties of silica gel phases-immobilized-amine derivatives, *Anal. Chim. Acta.* 525 (2004) 123–132.