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RESEARCH ARTICLE

Separation and Determination of Cd^{2+}, Pb^{2+} and Cu^{2+} from Water Samples Using Chemically Modified Groundnut Shells

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Abstract

Chemically modified groundnut shells via esterification with Tartaric acid under conditions were employed and used as a new solid phase extraction (SPE) sorbent for determination of trace metals as Cd^{2+}, Pb^{2+} and Cu^{2+} from environmental water samples. Experimental conditions for effective separation and preconcentration of the studied metal ions were optimized with respect to different experimental parameters in batch and column processes. Tartaric acid groundnut shells sorbent (TA-GNS) was characterized by FT-IR, SEM and TGA analysis. Optimal experimental conditions were at pH 6, shaking time 60 min, sample flow rate 4 $mL.min^{-1}$ and desorption by 12.5 mL from 1.0 $mol.L^{-1}$ HCl. The limit of detection was found to be 0.72, 0.64 and 1.6 $\mu g.L^{-1}$for Cd^{2+}, $Pb^{2+}$and Cu^{2+} respectively. A preconcentration factor of 160 has been achieved for all studied metal ions.Precision (R.S.D %) was also evaluated and found to be $\leq$ 6.0 % (n=3).The potential applications of the modified TA-GNS for the removal and separation of the examined metal ions from two water samples (tap water and treatment plant water intake (New El-Azab) at Fayoum City, Egypt) were investigated.

Introduction

The determination of heavy metals, especially some toxic metals that play important roles in biological mechanisms, has been receiving much attention. Lead enters the organism primarily via the alimentary and/or the respiratory tract. The main sources of this metal intake are food, air and drinking water [1]. The major effects of cadmium poisoning are experienced in the lungs, kidneys and bones [2].Copper causes "Wilson's disease" where excess copper is deposited in the brain, skin, liver, pancreas, and myocardium [3]**.**Briefly, it is seen that these three metals can dangerously affect human health even at ultra-trace concentrations. In recent years, a number of promising techniques for the determination of heavy metal ions including atomic absorption spectrometry (AAS)[4] and inductively coupled plasma optical emission spectrometry(ICP-OES)[5,6,7]have been reported. The direct determination of trace metal ions by modern techniques is often difficult due to low concentrations and matrix effects. Therefore, the separation and preconcentration of trace metal ions is often required [8, 9].Nowadays, various separation/enrichment techniques have been used to improve the sensitivity and selectivity of trace analyses. In the light of the above facts, accurate determination of toxic metals has become increasing which is necessary to solve the problem connected with environmental water pollution. Many attempts have been reported to sorb metal ions by cheaper materials like natural products / biological wastes [10, 11]. Many crops generate considerable quantities of shells each year but this has little or no value. There is a need to convert these by-products into useful ones. There are several reports denoting that peanut shells can be used as low cost biosorbent[12]. Biopolymers like groundnut shells are of special interest and promising for a number of reasons. Biopolymers are capable of removing metal ions to ppb levels; they are cheap, abundant and environmentally safe. Another attractive feature of biopolymers is that they possess a variety of functional groups, which also includes hydroxyl groups such as tannin and lignin believed to be the active sites for the attachment of heavy metal ions[13]. When chemically modified the cellulosic biomaterial gives an enhancement in their adsorptive capacity for metal ions[14]. These purified biopolymeric materials like saw dust and groundnut shells possess both cellulose and lignin as major components [15].Kiran B.M has reported that the biosorption has distinct advantages over the conventional methods. This includes reusability of biomaterial, low operating cost, selectivity for specific metal, short operation time through study on the utilization of groundnut shell as biosorbant for heavy metals removal from aqueous solutions[16]. N.Burham has reported separation and preconcentration system for lead and cadmium determination in natural samples using modified polyurethane foamas low cost sorbent [17]. M.A. Khan has investigated the biosorption of Ni(II) on Oil cake by both batch and column processes[18]. R.Leyva-Ramos has studied the effect of the concentration of citric acid on the Cd(II) adsorption capacity of corncob[19]. The purpose of this study is to develop a new sorbent with good metal ion extraction characteristics from the low cost groundnut shells via esterification with tartaric acid under conditions to be employed as a modification method. The resulting TA-GNS sorbent is evaluated for separation and preconcentration of Cd^{2+}, Pb^{2+} and Cu^{2+}.

2. Experimental

2.1. Instrumentations

Flame atomic absorption spectrometric (FAAS) measurements of Cd^{2+},$Pb^{2+}$and Cu^{2+}were recorded on PerkinElmer AAnalyst 100 instrument (USA).The operational conditions for the measurements are depicted in Table 1.The FAAS method was used for the determination of the studied metal ions. The pH measurements were carried out using UB-5 Denver pH meter (Colorado, USA), GFL 3018 mechanical shaker (Burgwedel, Germany) was used for shaking the samples. Millipore water purification system (Molsheim,France) was used for the production of deionized water. Eppendorff automatic pipettes (Germany) of different ranges were used to deliver accurate volumes.

2.2. Chemicals and solutions

All reagents used were of analytical grade. The stock solutions of 1000 mg.L^{-1} concentration from studied metal ions were prepared by dissolving appropriate amounts of $Pb(NO_3)_2$(Aldrich ,USA), $Cd(NO_3)_2.4H_2O$(Panreac,Spain) and $CuSO_4.5H_2O$ (Aldrich) in deionized water. Tartaric acid (BDH, England) was used for the modification. Sodium hydroxide (Merck,Germany) and hydrochloric acid (BDH) were used for pH adjustments.

2.3. Preparation of Groundnut shells (GNS) sorbent

Groundnut shells (GNS) used in this study were obtained from a local market in Fayoum city (Egypt). First, the collected biosorbent was extensively washed with tap water to remove dust, sprayed with deionized water, and washed with 0.1 mol L^{-1} HCl. Next, the GNS were washed with deionized water till the filtrate free from chloride ions. Then, the shells were dried in an oven at 60 ^{o}C till they reached a constant weight. After that, the dry sorbent was crushed into powder and sieved by AS 200 sieve shaker (Germany) to different particle sizes. The GNS of uniform size (250-500µm) was taken for modification.100 g of GNS were mixed with a certain weight of tartaric acid in mortar and a little amount of water was added under continuous mixing until a homogenous paste was obtained. The paste was transferred to a Pyrex petridish and dried at 100 ^{o}C for 3 h. The treated sample was cooled to room temperature and then grounded. Soluble by-products and untreated acid were removed by extraction with water / ethanol mixture (20/80) in a soxhlet for 5 h. Finally the purified material was dried at 60 ^{O}C for 2 h.

2.4. Recommended procedures.

2.4.1. Batch procedure

The effect of sample pH on the sorption of TA-GNS sorbent and the unmodified GNS were investigated using a 25 mL solution containing 125µg of Cd^{2+}, Cu^{2+} and 500 µg of Pb^{2+} in individual metal ion solutions within pH range 2 - 8. The pH of the solutions was adjusted with HCl or NaOH. Each solution was shaken in a mechanical shaker with 0.1 g of the GNS in 125 mL polyethylene bottle for 1 h. After the equilibration, the remained metal ions were determined by FAAS. The effect of shaking time on the sorption (%)was carried out at different shaking time intervals from 10 to 100 minat 200 rpm. The percentage of sorption (%) was determined using the following formula: Sorption (%) $=[(C_0-C)/C_0]\times 100$,where C_0 and C are the initial and the remaining concentration of the metal ion respectively. Sorption isotherm was measured by shaking different concentrations of metal ions with the sorbent. Typically, 0.2 g of TA-GNS sorbent was equilibrated with 0.375 – 3.75 mg metal ions in 25 ml solution adjusted to pH 6. The maximum capacity Q (mg/g) was calculated from the equation: $Q = [(C_0-C) \times V]/m$, where V is the sample volume in liter and m is the weight of TA-GNS sorbent in (g).

2.4.2 Column procedure

In the dynamic experiments, 1.0 g of TA-GNS sorbent was packed into a glass column (30×1.5 cm). A small amount of glass wool was placed at both ends of the column to prevent the loss of the sorbent duringthe flowing of the sample through the column. It was washed successively with deionized water. The test solutions were passed through the modified TA-GNS column at a flow rate of 4 $mL.min^{-1}$. Preconcentration of the studied metal ions was investigated within the volume range 25-2500 mL solution at metal ion concentration from 0.02 to 2 $\mu g.mL^{-1}$.The stripping of the retained metal ions in the column was carried out with 1 $mol.L^{-1}$HCl eluting agent and the amount of the metal ion in the eluate was determined.

2.5. Samples preparation

Two samples, two- liter volume of each, were collected from tap water of our central laboratories in Fayoum Drinking Water and Sanitation Company in Fayoum city and the intake of the water treatment plant (New El-Azab). The water samples were collected in 2-liter polyethylene bottle, filtered through 0.45µm cellulose-acetate membrane filter, spiked with 50 µg of the metal ions, adjusted to the optimum conditions and passed through the modified TA-GNS column. The metals were eluted by 1 $mol.L^{-1}$HCl. The concentration of each metal ion was determined by the recommended method.

3. Results and discussion

3.1. Characteristics of GNS

The physical and chemical characteristics of GNS used as adsorbent in this study [20] were summarized in Table 2. Groundnut shells contain cellulose in significant amounts. Cellulose is a natural polymer made of β-D-glucose repeating units and contains abundant primary and secondary hydroxyl groups. Lignin contains majority of methoxy and free hydroxyl groups. Both these chemical entities are capable of adsorbing various metal ions [21]. The adsorption of metal ion on these materials has been shown to be of ionic nature and even dilute acids that are capable of desorbing the metal ions fully [15].

3.1.1. FT-IR Analysis

FT-IR spectrum of the modified TA-GNS sorbent is represented in Fig 1. It shows that characteristic absorption band has appeared with increasing intensity of the absorption band at 3402-3426 cm^{-1} and absorption band at 2923-2934 cm^{-1}, which refers to the bonded OH in carboxylic group,absorption bands at 1400 -1731 cm^{-1} indication of (-COOH , COO and C=O) and the presence of the band at 1036 cm^{-1} refers to CH_2-OH. FTIR spectrum shows that the GNS are mainly composed of polymeric OH groups, CH_2 and COOH groups and OH of poly saccharides. These groups have affinities of Cd, Pb and Cu ions extraction.This figure shows that the function groups of GNS become of high availability for adsorption than unmodified GNS.

3.1.2 Scanning Electron Microscope Analysis [SEM]

In Fig 2,SEM photographs of the modified TA-GNS (A) and the unmodified GNS (B) indicate some imperfections on the surface of the GNS wall verified after treatment with tartaric acid. Thus, it can be concluded that, the modified TA-GNS present an adequate morphological profile to retain the studied analyte ions. These results are in agreement with those obtained for other biomass, which are basically composed of lignin, cellulose and hemicellulose. Therefore, the SEM photographs show good progressive changes in the surface of the modified TA-GNS sorbent.

3.1.3 Thermal Gravimetric Analysis [TGA]

This analysis indicates the mass loss related to moisture elimination, cellulose, hemicellulose, and lignin decomposition. Fig 3 presents TGA curve for the modified TA-GNS. Thus, the moisture loss is 7.50 % by heating TA-GNS sample up to 200^oC. The second step is pyrolysis corresponding to temperature from 200 – 340 ^oC. This step provides higher mass loss of 49.9% for the modified TA-GNS sorbent. The pyrolysis curve in this temperature range refers to cellulose and hemicellulose decomposition, as well as the loss of remaining adsorbed water. Lignin was decomposed in temperature range 340- 580 ^oC, which is due to the higher stability of lignin composed to cellulose and hemicellulose. The mass loss in this step was 40.8% for modified TA-GNS sorbent. Finally, no mass loss was observed when the temperature was increased up to 700 ^oC.

3.2. Batch procedure

3.2.1. Effect of sample pH

The pH of the solution has been found to be the most important one. It not only influences the speciation of the extracted ions, but also the charges on the biomass sites [22]**.** So, it is important to consider the ionic states of the functional groups of the modified TA-GNS sorbent as well as the metal ions solution chemistry at different pH values. For example, the ionization constant of various carboxyl groups has been reported to be around 3-4[23]. In highly acidic pH values, these are protonated and act as positively charged species[24]. Thus an appropriate pH value can not only improve the sorption efficiency, but also depress the matrix interference. The interactions of the metal ions with the GNS surface are complex. This extraction process was dominated by adsorption, ion exchange and chelation. The binding of metal ions involved two mechanisms, the first of these being simple ion exchange and the second through the formation of complexes, which may be chelates [23]. According to that, the adsorption will lead to decrease the pH as equivalent hydrogen ions will be released along with the adsorption [25]. Because of the complexity of GNS as a biomass, it is very likely that both ion exchange and complex formations will take place in the system at the same time. The lignocellulosic materials in the GNS accomplished the requirements for a good adsorbent.

It is clear from Fig 4A that at lower pH the adsorption of the studied ions are extremely reduced except for Pb^{2+} extraction on the TA-GNS sorbent. The optimum pH value is taken at pH 6. The percentage uptake reached 90%, 95% and 94% for Cd^{2+}, $Pb^{2+}$and Cu^{2+} respectively. Also, Fig 4B shows the maximum extraction for theunmodified GNS sorbent at pH 7 as the optimum pH. The percentage uptake reaches 57.5%, 55% and 56% for Cd^{2+}, Pb^{2+} and Cu^{2+} respectively.

As the pH increases from the highly acidic to slightly acidic region, the positive character of the GNS converts to a negative one. Then, the GNS starts attracting the positively charged tested ions. Certain function groups such as amino group contain lone pairs of electrons and thus can contribute towards the formation of coordinate bonds with Cd^{2+}, $Pb^{2+}$and Cu^{2+} ions. This complexation process is highly pH dependent and occurs only at some specific pH values. Thus, any change in the pH value could affect the complexation and cause a change in the extraction efficiency of the GNS as biomass.

Fig 1. FT-IR spectra of the modified TA-GNS.

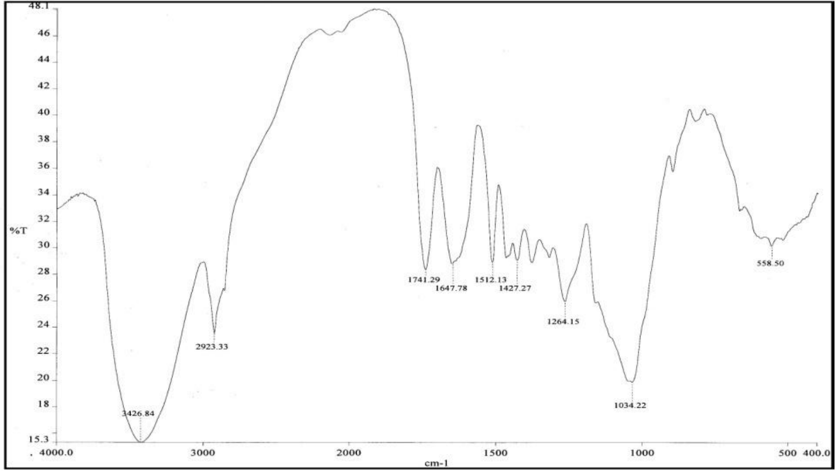

Fig 2. Scanning electron micrographs for (A) modified TA-GNS and (B) the unmodified GNS

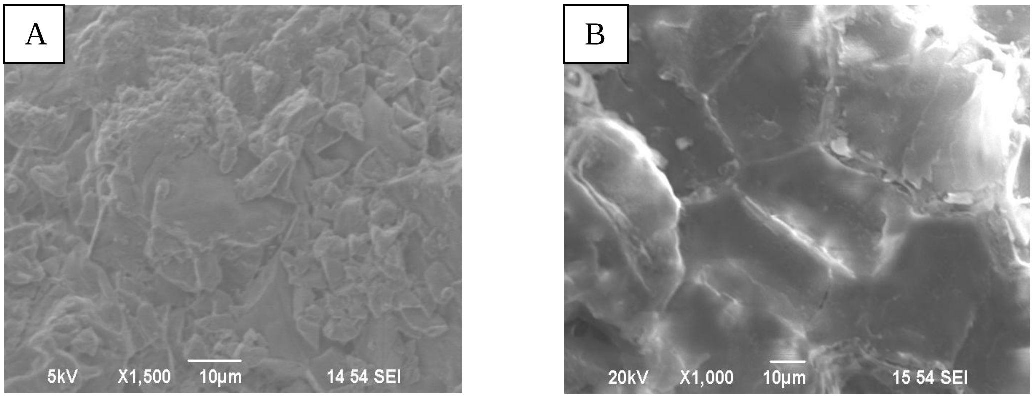

Fig 3. TGA curve for the modified TA-GNS

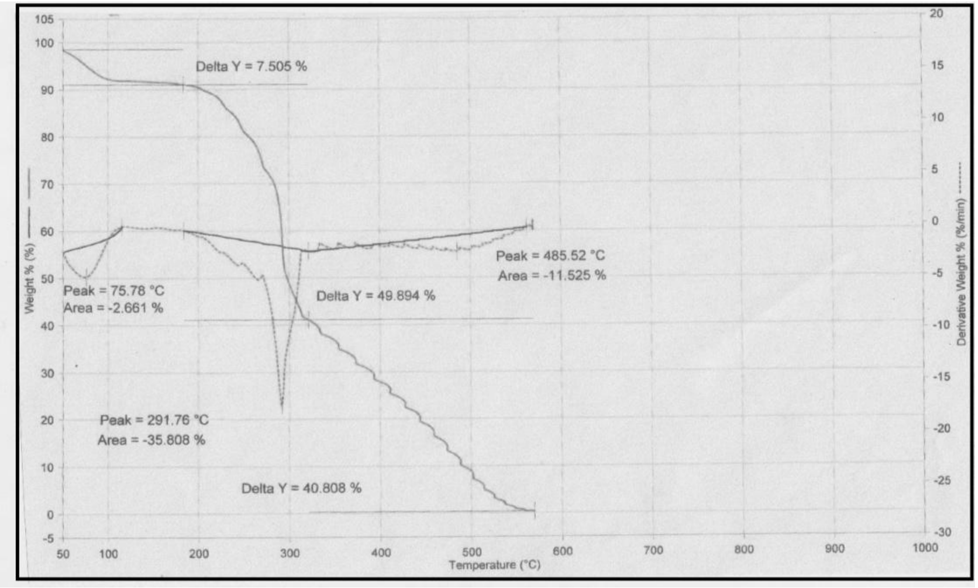

Fig 4. Effect of sample pH on the extraction of Cd^{2+}, Pb^{2+} and Cu^{2+} with (A) the modified TA-GNS and (B) the unmodified GNS.

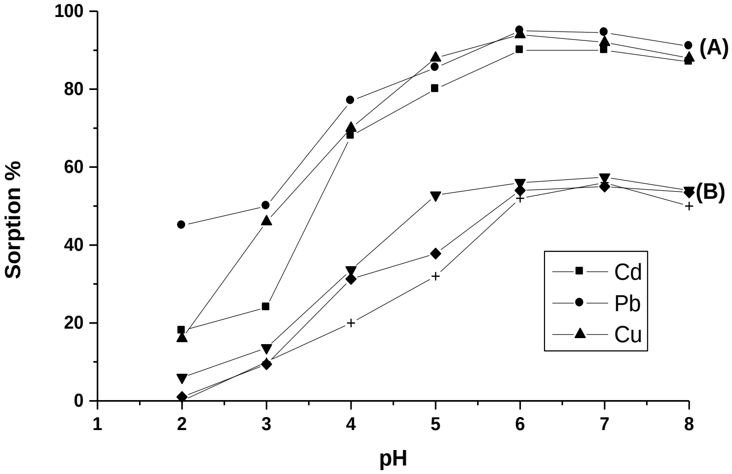

Fig 5. Effect of shaking time on the extraction of Cd^{2+}, Pb^{2+} and $Cu^{2+}$with (A) the modified TA-GNS and(B) the unmodified GNS.

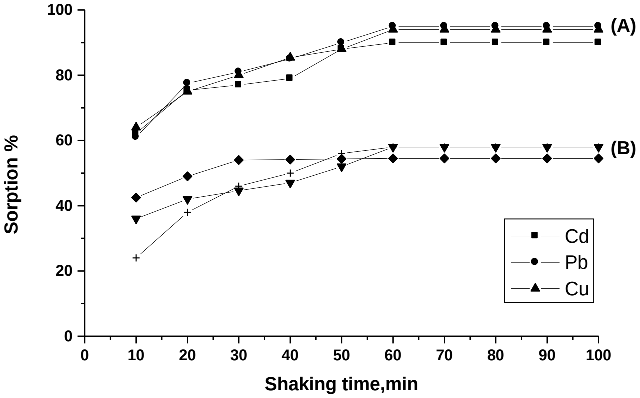

Fig 6. Extraction isotherm of Cd^{2+}, Pb^{2+} and $Cu^{2+}$with the modified TA-GNS.

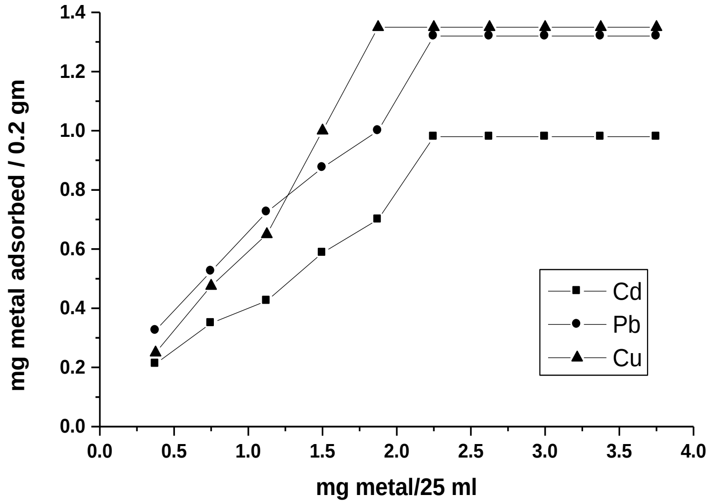

Fig 7. Breakthrough capacity of Cd^{2+}, Pb^{2+} and $Cu^{2+}$with the modified TA-GNS.

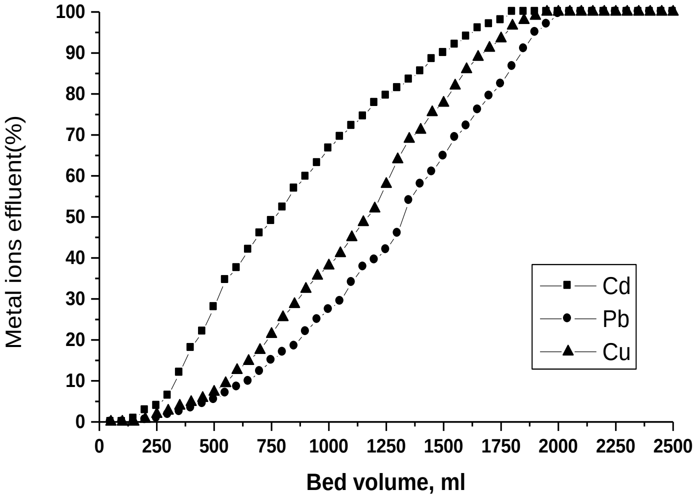

Table 1.Operational conditions for the measurementsCd^{2+}, Pb^{2+}& Cu^{2+} with FAAS

	Cd^{2+}	Pb^{2+}	Cu^{2+}
Lamp type	EDL[1]	EDL	HCL[2]
Lamp Current (mA)	210	430	30
Slit width (nm)	0.7	0.7	0.7
Wavelength (nm)	228.8	283.3	324.8
Recommended Flame	Air- Acetylene		
Burner head (cm)	10	10	10

[1] EDL : Electrodeless Discharge Lamp

[2] HCL : Hollow Cathode Lamp

Table 2. Physical and chemical characteristics of GNS.

Physical characteristic		Chemical characteristic	
Bulk density	80 –112 Kg/m^3	Cellulose	65.7 %
Porosity	61- 70 %	Carbohydrates	21.5 %
Adsorbent pH	6.7	Protein	7.3 %
		Lignin	27 - 33 %
		Fiber	60 -70 %
		Moister	8 - 10 %
		Ash	2 - 4.5

Table 3.Tolerence limits of some interfering ions.

Interfering ions	Tolerance limit (mg/l)		
	Cd^{2+}	Pb^{2+}	Cu^{2+}
Na^+	210	2700	400
K^+	350	1600	450
Ca^{2+}	210	510	360
Mg^{2+}	200	490	440
Cl^-	900	2200	800
SO_4^{2-}	670	1900	850

Table 4. Preconcentration factor of the tested analyte on the modified TA-GNS

Metal ions	Initial volume ml	Final volume ml	Recovery %	CF[1]
Cd^{2+}	2000	12.5	96%	160
Pb^{2+}	2000	12.5	98%	160
Cu^{2+}	2000	12.5	97%	160

[1] CF: concentration factor

Table 5. Analysis of spiked water samples with modified TA-GNS sorbent, (n = 3)

Sample	Metal ions	Without spiking	Spiked µg	Found µg (Mean± S.D)	Recovery %	R.S.D%
Tap water	Cd^{2+}	ND[1]	50	49.2±1.82	98	3.7
	Pb^{2+}	ND[1]	50	48.9±1.71	97	3.5
	Cu^{2+}	5 µg	50	57.0±2.79	103	4.9
Intake of water treatment plant (New El-Azab)	Cd^{2+}	ND[1]	50	48.9±2.01	97	4.1
	Pb^{2+}	ND[1]	50	48.9±2.54	97	5.2
	Cu^{2+}	10 µg	50	61.5±3.69	102	6.0

[1]ND: Not detected [2]S.D: Standard deviation

Table 6.Comparison with other extractors

Extractor	Studied metals	pH	Eluent	Flow rate mL min^{-1}	CF	LOD	Ref.
Ambersorb 563	Cd , Pb	8-10	0.25 mol.L^{-1} HNO_3	5	125	0.33,72 µg/l	**[27]**
AmberliteXAD-2000/8-hydroxyquinoline	Cd , Pb	6	1mol.L^{-1} HNO_3 in acetone	10	100	0.3- 2.2 µg/l	**[28]**
DiaionSP-850/Alpha-benzoin oxime	Cd , Pb	8	1 mol.L^{-1} HNO_3	5	50	0.28- 0.73 µg/l	**[29]**
Modified TA-GNS	Cd , Cu , Pb	6	1 mol.L^{-1} HCl	4	160	0.72,1.6,0.64 µg/l	**This work**

3.2.2. Effect of shaking time

Typical biosorption kinetics exhibit a rapid initial extraction, followed by a slower process especially for $Cd^{2+}$and Pb^{2+}. InFig 5A, the results obtained indicate that equilibrium extraction of the TA-GNS sorbent for Cd^{2+}, Pb^{2+} and Cu^{2+} is attained at 60 min, whereasthe unmodified GNS indicated that equilibrium extraction of Cd^{2+}, Pb^{2+} and Cu^{2+} ions are attained after 60 min as shown in Fig 5B**.**

The relatively faster sorption of Cd^{2+}, $Pb^{2+}$and Cu^{2+}ions probably reflects a better accessibility of the tested ions on the active sites built on the GNS through the modification and strong bond formation with these sites. The result shows that a 60 min sorption period is the best option to ensure the metal extraction from the solution.

3.2.3. Sorption Capacity

The relationship between the amount of the substance extracted at a constant temperature and its initial concentration in the equilibrium solution is called the adsorption isotherm Fig 6.The extraction capacity of the modified TA-GNS sorbent toward the tested ions is determined after establishing the optimum conditions for the pH and shaking time, followed by measuring equilibrium isotherms Fig 6.The capacity of the modified TA-GNS sorbent is found to be 4.9,6.6 and 6.75 mg.g^{-1}for Cd^{2+}, $Pb^{2+}$and Cu^{2+} respectively, whereas the capacity of the unmodified GNS is found to be 2.63,2.00 and 2.25 mg.g^{-1} for Cd^{2+},Pb^{2+} and Cu^{2+},respectively. This confirms that the new modified TA-GNS sorbent has a greater affinity toward these metal ions than the unmodified GNS.

3.2.4. Effect of interfering ions

The effects of common interfering ions on the adsorption of the studied metal ions were investigated. A number of works [26] have intensively investigated this effect. In general, sorption decreases with increasing the ionic strength of the solution. A species is considered to interfere when it effects on the sorption of metal ion by ±5 error .The tolerance limits of various foreign ions i.e. sodium, potassium, calcium, magnesium, chloride and sulfate on the sorption of lead, cadmium and copper ions at ±5 error are studied and was given in Table 3. Results indicate that, the extraction on the modified TA-GNS sorbent is not much sensitive to the tested species. This result showed that the extraction of the studied ions was not affected by the medium composition. Before these limits there is no significant decrease in the extraction of lead, cadmium and copper, indicating that, the new proposed method could be applied for the preconcentration, extraction and determination of the analyte ions in real water samples.

3.3. Column procedure

3.3.1. Effect of Sample flow rate

Sample flow rate is a measure of the contact time between the metal ions in the liquid phase and the solid sorbent. The lower the flow rates, the longer the contact time and the larger extent of metal binding are. An aliquot of 25 mL at concentration 10 mg.L^{-1} from each metal ion was adjusted at pH 6 and introduced to the modified TA-GNS column at varying rates from 2 - 20 ml.min^{-1} and the tested metal ions was eluted by 1 mol.L^{-1} HCl and determined by FAAS method. According to the experimental results, it is found that the recovery of Cd^{2+}, Pb^{2+} and Cu^{2+} reached 93%, 98% and 96% for Cd^{2+}, Pb^{2+} and Cu^{2+} respectively at flow rate 4 mL.min^{-1}. A sample flow rate of 4 mL.min^{-1} is adopted as the optimum for the metal ions retention.

3.3.2. Elution of metal ions

The effect of eluent concentration on the desorption of the metal ions was studied with 25 mL of hydrochloric acid solution at varying concentration between 0.01 - 1.5 mol.L^{-1} HCl and 1.0 mL.min^{-1} flow rate. Also, the volume of eluent is necessary to quantitatively remove these elements from the sorbent. It is important to use sufficient volume from the eluent; however, extra volume will adversely affect the value of preconcentration factor. Elution was effected with volumes from 2.5 to 25 mL . The results showed that 12.5 mL of 1.0 mol.L^{-1} HCl solutions are suitable to elute the studied metal ions quantitatively (≥ 96%) from the modified GNS.

3.3.3. Breakthrough capacity

The dynamic capacity of the column is computed by percolating it with individual metal ions solution with concentration 10 mg.L^{-1} and pH 6 at flow rate 4 mL/min. From Fig 7,it is clear that the steep curve at the breakthrough point for the three metal ions on the modified TA-GNS column suggests the better ability of the modified sorbent for the separation and preconcentration of Cd^{2+},Pb^{2+} and Cu^{2+}.The capacity of the modified column are estimated to be 7.5 ,13.15,11.75 mg.g^{-1} respectively. It is obvious that the extraction capacity of the novel modified TA-GNS is generally good. It can be used to extract Cd^{2+}, Pb^{2+} and Cu^{2+} from dilute aqueous solution.

3.3.4. Preconcentration

The effects of sample volume are examined in the range of 25-2500 mL. The preconcentration factor is calculated from the ratio of the initial volume to the final eluted volume. The results are shown in Table 4.The extraction of the analyte ions is quantitative in the sample volume range 25-2000 mL. The preconcentration factor is 160. The new modified TA-GNS sorbent is one of the effective multielement preconcentration extractors since it can provide more flexible working conditions together with good stability, selectivity and high capacity. The results show that Cd^{2+}, Pb^{2+} and Cu^{2+} can be concentrated effectively from dilute solution using the modified TA-GNS sorbent column.

3.3.5 Limit of detection

The limit of detection (LOD) is defined as blank concentration +3σ where σ is the standard deviation of the blank determination. The proposed method for the determination of Cd^{2+}, Pb^{2+} and Cu^{2+} was studied under the optimum experimental conditions. The detection limits were established by analyzing 7 blank solutions. The LOD of Cd^{2+}, Pb^{2+} and Cu^{2+} are found to be 0.72, 0.64 and 1.6 µg.L^{-1} respectively. The LOD values for Cd^{2+}, Pb^{2+} and Cu^{2+} with the new modified TA-GNS sorbent enable the use of this extractor in collection of the tested ions of trace concentration prior to their determination with high accuracy.

3.4. Analysis of water samples

All of the previous determined optimum parameters were taken into account in the preconcentration of the studied metal ions in real water samples. The new proposed method was applied to the determination of the studied metal ions in tap water sample and the intake of water treatment plant(New El-Azab).The standard addition method was applied to check the selectivity of the modified TA-GNS sorbent for the analyte ions against different matrices to determine the accuracy and the precision of the new extraction method. The water samples spiked with 50 µg for each studied metal ions ,then the water samples was passed through the column at flow rate 4 ml. min^{-1}.The studied metal ions were eluted with 12.5 ml 1 $mol.L^{-1}$ HCl and the metal ion were determined by the established method. The results are shown in Table 5. The recoveries in all samples are remarkably high. This indicate the high selectivity of the modified sorbent toward Cd^{2+},Pb^{2+} and Cu^{2+} .The relative standard deviation (R.S.D%) of three replicates is ≤ 6 % indicates that the proposed method is a highly precise.

4. Comparison with other extractors.

A comparison of the proposed system with other procedures is given in Table 6**.**As seen from the data in Table 6, the proposed method developed by using the modified TA-GNS system has the high preconcentration factor when compared to other methods.

5. Conclusions

The modified biomass groundnut shells (TA-GNS) via esterification method using tartaric acid has been successfully utilized as a solid phase extractor for separation, preconcentration and determination of cadmium, lead and copper from real water samples. The new sorbent shows several good characteristics such as higher extraction capacity forCd^{2+},Pb^{2+} and Cu^{2+}, more accuracy and precision than the unmodified GNS. Preconcentration factor reaches 160.

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