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RESEARCH ARTICLE

Solid phase extraction method for the determination of Cd^{2+}, Pb^{2+} and Cu^{2+}in different water samples by flame atomic absorption spectrometry using green modified groundnut shells.

N. Burham[1], A.Mamdouh[2]*, M.F.El-Shahat[3]

1. Chemistry Department, Faculty of Science, Fayoum University, Fayoum City, Egypt
2. Central Laboratories, Fayoum Drinking Water and Sanitation Company, Fayoum City, Egypt
3. Chemistry Department, Faculty of Science, Ain-Shams University, Cairo, Egypt

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***Corresponding Author**

A.Mamdouh

Abstract

A novel modified biomass (GNS) has successfully been utilized as a new solid phase extraction (SPE) sorbent for the determination and preconcentration of cadmium, lead and copper in aqueous medium. The batch procedure shows the maximum extraction percentage on the GNS modified with sodium carbonate (SC-GNS) are 100, 98 and 96% for Cd^{2+}, Pb^{2+} and Cu^{2+}ions, respectively, at the optimal conditions pH 4-6 and 30 min shaking time .The column procedure shows that the optimal conditions were at sample flow rate 4 $mL.min^{-1}$ and desorption by 10 mL from 1.0 mol L^{-1} hydrochloric acid. The breakthrough volume was greater than 2000 ml with preconcentration factor 200 for all studied metal ions .The limit of detection was found to be 0.28 ,0.48 and 1.2 for Cd^{2+}, Pb^{2+} and Cu^{2+}ions, respectively. Precision (R.S.D %)of the metal ions extraction was found to be less than 5 %(n=3). The developed method was successfully applied for determination of these metal ions in different water samples (tap water, intake of water treatment plant and Qaroun lake at Fayoum city, Egypt) by flame atomic absorption spectrometry (FAAS).

1. Introduction

The toxic metals pollution in natural water has been receiving tremendous attention, and are capable of causing ecological risk to the aquatic organism, their minor content can bio-accumulate and enter the food chains causing mental retardation, reduction in hemoglobin production, interference with normal cellular metabolism and consequently may damage nervous system. Strong exposure may cause gastric pain, nausea, severe diarrhea and even cancer in the digestive tract and lungs [1]**.** Briefly, it is seen that these metals can dangerously affect human health even at ultra-trace concentrations. Due to these reasons, the accurate and precise determination of trace metals ions is important for analytical chemists [2]. Various analytical techniques have been using such as atomic absorption spectroscopy (AAS), inductively coupled plasma and plasma emission spectroscopy [3]**.**In trace element analysis, preconcentration and separation step is needed to enhance the sensitivity and precision of the determination. The presence of trace heavy metals lower than the detection limits of the instrumental techniques is one of the main problems at these low levels. Therefore, preconcentration techniques including liquid-liquid extraction, cloud point extraction, co-precipitation and solid phase extraction are generally used to solve this problem [4, 5]. Solid-phase extraction (SPE) may be used as an alternative technique to improve the sensitivity and selectivity of FAAS. In addition, it has some extra advantages: large availability, easy recovery of the solid phase, attainability of large preconcentration factors and facility for separation, based on the use of sorbent materials for column packing such as amberlite or Chelex [6], activated carbon **[7]** polyurethane foam (PUF) [8, 9] and low cost adsorbents [10, 11].The groundnut shells have been successfully used as low cost biosorbent [12] to sorb metal ions.Many attempts have been reported that sorption by these cheaper materials like natural products / biological wastes [13, 14], converted into activated carbon and used to adsorb various pollutants [15, 16]. Shulka studied the potential of groundnut shells and sawdust for Cu(II),Ni(II) and Zn(II) adsorption from aqueous solution[17]**.**Kiran B.Mhas reported that the biosorption has distinct advantages over the conventional methods, which include reusability of biomaterial, low operating cost, selectivity for specific metal, short operation time through study on utilization of groundnut shell as biosorbent for heavy metals removal from aqueous solutions [18].

Biopolymers like groundnut shells are capable of removing metal ions to ppb levels, they are cheap, abundant and environmentally safe. The adsorption technique is one of the preferred methods for the removal of heavy metals because of its efficiency and low cost. In view of the above facts, accurate determination of toxic metals has become increasing necessary to solve the problem connected with environmental water pollution. Another attractive feature of biopolymers is that they possess a variety of functional groups, which also includes hydroxyl groups, such as tannin and lignin, which are believed to be the active sites for the attachment of heavy metal ions [19].Lignin molecule is built up from phenyl propane nucleus, i.e. an aromatic ring with three carbon side chains, all those components are active ion exchange compounds and have been shown to sorb metal ions from their aqueous solution. These moieties can be reacted for possible enhancement in the efficiency of metal ion uptake. The cellulosic biomaterial when chemically modified gives an enhancement in their adsorptive capacity for metal ions [20]. And these purified biopolymeric material like saw dust and groundnut shells possess both cellulose and lignin as major components [21]. The purpose of this study is to develop a new sorbent with good metal ion extraction characteristics from the low cost groundnut shells using a simple modification method with the safe and cheap sodium carbonate to achieve a simple preconcentration system that allows determination of the studied ions at concentration within the μg/l range.

2. Experimental

2.1. Instrumentations

Flame atomic absorption spectrometry(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. Sodium carbonate (BDH, England) was used for the modification. Sodium hydroxide (Merck, Germany) and hydrochloric acid (BDH) were used to pH adjustments.

2.3. Preparation of Groundnut shells (GNS) sorbent

Groundnut shells (GNS) was 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 was free from chloride ions. Then the shells were dried in an oven at 60 °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. A uniform size (250-500μm) was taken for modification .For this purpose, 100 g GNS was soaked with stirring in one liter of 0.5 mol sodium carbonate for 24 h.The treated GNS was thoroughly washed with deionized water to the neutral pH, then filtered and dried at 60 °C.

2.4. Recommended procedures

2.4.1. Batch procedure

The effect of sample pH on the sorption of the modified SC-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 effect ofsorbent weight on the sorption (%) was carried out at different sorbent weight 0.05 g to 0.4 g.The percentage of sorption (%) was determined by using the following formula: Sorption $\%=[(C_0-C)/C_0]\times100$, 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 the modified SC-GNS 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 SC-GNS sorbent in (g).

2.4.2. Column procedure

In the dynamic experiments, 1.0 g of the modified SC-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 SC-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 µg/mL.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

Three samples, two- liter volume of each, were collected from tap water of our central laboratories in Fayoum Drinking Water and Sanitation Company, intake of the water treatment plant (New El-Azab) and Qaroun Lake at Fayoum city, Egypt. 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 SC-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. Batch procedure

3.1.1. Effect of sample pH

Among all other parameters, the pH of the solution is one of the most important one. It not only influences the hydrolysis of the metal 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 GNS as well as the metal ions solution chemistry at different pH values. The ionization constant of various carboxyl groups in GNS has been reported to be around pH 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 Cu, Cd and Pb ions with the modified and unmodified groundnut shells 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 are accomplished requirements for good adsorbent. It is clear from **Figure 1(A**) that, at lower pH the sorption of the studied ions was extremely reduced except for Pb^{2+}. Quantitative sorption for all the metal ions was reached 100%, 98.2% and 96.2% for Cd^{2+}, $Pb^{2+}$and Cu^{2+} respectively and the optimum pH value was found at pH 4-6.Whereas **Figure 1(B)** shows that, the percentage sorption for the unmodified GNS was reached 57.5%, 55% and 56% for Cd^{2+}, Pb^{2+} and Cu^{2+} respectively at pH 7 as the optimum value.As the pH is increased from the highly acidic to slightly acidic region, the positive character of the GNS is converted 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 to the formation of coordinate bonds with metal 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.Generally, when the solution pH exceeds 8, the metal ions may be precipitated out making it the upper limit of the pH range to be studied.

3.1.2. Effect of shaking time

A typical sorption kinetics exhibit a rapid initial extraction, followed by a slower process especially for $Cd^{2+}$and Pb^{2+}**.** In **Figure 2(A)**, the results obtained indicate that equilibrium state of the modified SC-GNS sorbent for Cd^{2+}, $Pb^{2+}$was attained at 30 min, whereas equilibrium extraction for Cu^{2+} was attained after 60 min. In **Figure 2(B)**, the sorption equilibrium of the unmodified GNS was attained after 60 min for all the studied metal ions. The relatively faster sorption of metalions probably reflects a better accessibility of the tested ions on the active sites bilt on the GNS through the modification and strong bond formation with these sites. The result showed that a 60 min shaking period was enough to ensure the attaining of equilibrium state.

3.1.3. Effect of sorbent weight

The sorbent dosage is an important parameter because this determines the capacity of the biomass for a given initial concentration. The effect of different dose of the modified and the unmodified GNS on the metal extraction of fixed amounts of metal ions in individual metal ion solutions was studied. Quantitative extraction of the tested ions required a minimum weight of the modified SC-GNS sorbent of 0.1 g for $Cd^{2+}$and Pb^{2+} to reach 100% and 99.2% respectively, whereas for Cu^{2+}0.15 g was needed to get sorption 95.5%. Whereas the maximum percentage sorption for the unmodified GNS reach 63.2%, 58.5% and68%for Cd^{2+}, Pb^{2+} and Cu^{2+} respectively at 0.25 g sorbent weight.

3.1.4. 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 **Figure 3**.The extraction capacity of the modified SC-GNS sorbent toward the tested ions was determined after establishing the maximum uptake in the isotherm Figure 3.The capacity of the modified SC-GNS sorbent was found to be 8.87, 9.37 and 8.125 $mg.g^{-1}$for Cd^{2+}, $Pb^{2+}$and Cu^{2+} respectively, whereas the capacity of the unmodified GNS was 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 modified SC-GNS has a greater affinity toward these metal ions than the unmodified GNS. Thus, the modified SC-GNS sorbent can be used as an alternative green and cheap solid phase extractor for the tested metal ions.

3.1.5. Effect of interfering ions

Foreign ions can influence the aqueous phase equilibrium [26] .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 on the sorption of lead , cadmium and copper ions at ±5 error are given in **Table 2**.sodium,potassium, calcium, magnesium, chloride and sulfate were studied. Results indicate that, the sorption on the modified SC-GNS sorbent is not much sensitive to the tested foreign species and were not affected by the medium composition. Also the tolerance limits of the coexisting ions are much higher than their concentrations found in natural water, indicating that, the new proposed method could be applied for the preconcentration and determination of the analyte ions in real water samples.

3.2. Column procedure

3.2.1. Effect of Sample flow rate

The sample flow rate is very important parameter since it controls the time of analysis. The retention of Cd^{2+}, Pb^{2+} and Cu^{2+} on to the modified SC-GNS column was studied at different flow rates varying from 2 - 20 $mL.min^{-1}$. The tested metal ions could be eluted by 1 $mol.L^{-1}$HCl and determined by FAAS method. According to the experimental results, the recovery of all metal ionsreached 100% at flow rate 4 $mL.min^{-1}$.Therefore, sample flow rate of 4 $mL.min^{-1}$ is adopted as the optimum for all metal ions.

3.2.2. Elution of metal ions

The effect of eluent concentration on the desorption of the analyte ions was studied with different concentrations of HCl in the range 0.01 - 1.5 mol.L^{-1}**Figure 4**. Also, the volume of eluent is necessary to quantitatively remove these metals 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 **Figure 5**. The results showed that 10 mL of 1.0 mol.L^{-1}HCl solutions are suitable to quantitatively elute the studied metal ions (≥ 97%) from the modified SC-GNS column.

3.2.3. Breakthrough capacity

The breakthrough capacity is more significant and useful than batch capacity in the modified SC-GNS column. From **Figure 6**.it is clear that the steep curve at the breakthrough point for the three metal ions suggests the better ability of the sorbent for the separation and preconcentration of these metal ions. The capacity of the modified column are estimated to be 11.6, 13.75, 12.25 mg.g^{-1} respectively. Obviously, the column capacity of the novel modified SC-GNS is generally good .It can be used to preconcentrate the metal ions from dilute aqueous media.

3.2.4. Preconcentration

The effects of sample volume were 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 3**.The extraction of the analyte ions is quantitative in the sample volume range 25-2000 mL. The preconcentration factor was calculated to be 200.The modified SC-GNS is one of the effective multielementpreconcentration extractors, since it can provide more flexible working conditions together with good stability, selectivity and high capacity. Finally this confirms that Cd^{2+}, Pb^{2+} and Cu^{2+} can be concentrated effectively from dilute solution.

3.3. Analytical performance

The limit of detection (LOD) is defined as blank concentration +3σ where σ is the standard deviation of the blank determination. The detection limits were established by analyzing 7 blank solutions. The LOD for Cd^{2+},Pb^{2+} and Cu^{2+} are found to be 0.28 ,0.48and 1.2 and the LOQ are 0.94 ,1.6 and 4.0 µg/l, respectively. The LOD values enable the use of this extractor in collection of the tested metal ions of trace concentration prior to their determination with high accuracy.

The reproducibility of the new method was evaluated by a model solution containing the target analytes with concentration of 50 µg (N=5). The relative standard deviation (R.S.D %) of the five determinations were below 1% as shown in **Table 4**.

To assess the accuracy of the proposed method, a standard reference solution traceable to NIST fromChem-lab-Spectro Econ (Belgium) and AA panreac (Spain) was analyzed by the developed method. The results are given in Table 4.Good agreement was obtained between the estimated concentration and the certified values. It is important to emphasize that the modified SC-GNS as a natural sorbent presents remarkable potential as a green preconcentration. In addition, it is negligible cost and no synthetic chelating agents used in this procedure with high accuracy making it alternative sorbent.

3.4 Analysis of water samples

The effect of matrices was studied in real water samples. The proposed method was applied to the determination of the studied metal ions in tap water sample, intake of water treatment plant (New El-Azab) and Qaroun lake. The standard addition method was applied to check the selectivity of the modified SC-GNS for the metal ions against different matrices to determine the accuracy and the precision of the new method. The water samples was spiked with 50 µg for each studied metal ions ,then it passed through the column at flow rate 4 mL.min^{-1}.The studied metal ions were eluted with 10 mL 1 mol.L^{-1}HCl and the metal ions were determined. The final results are shown in **Table 5**. A good agreement was obtained between the added and measured concentration of the metal ions. These results indicate good accuracy of the method. The relative standard deviation (R.S.D %) of three replicates is less than 5 %. These results showed that the proposed method give a high precision and can be used with high repeatability. The proposed modified extractor can be applied satisfactory for the determination of the tested ions from natural samples.

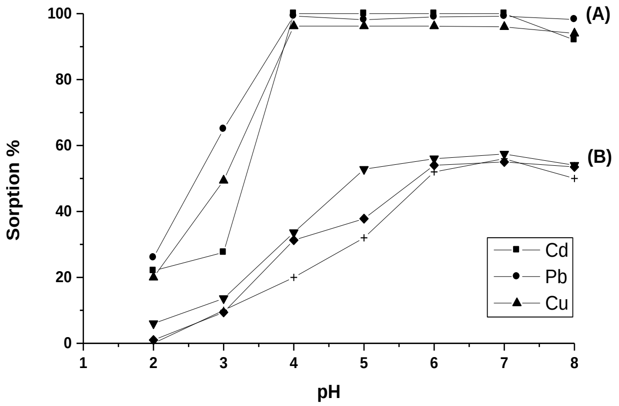

Figure 1. Effect of sample pH on the sorption of Cd^{2+}, Pb^{2+} and Cu^{2+} with (A) the modified SC-GNS and (B) the unmodified GNS.

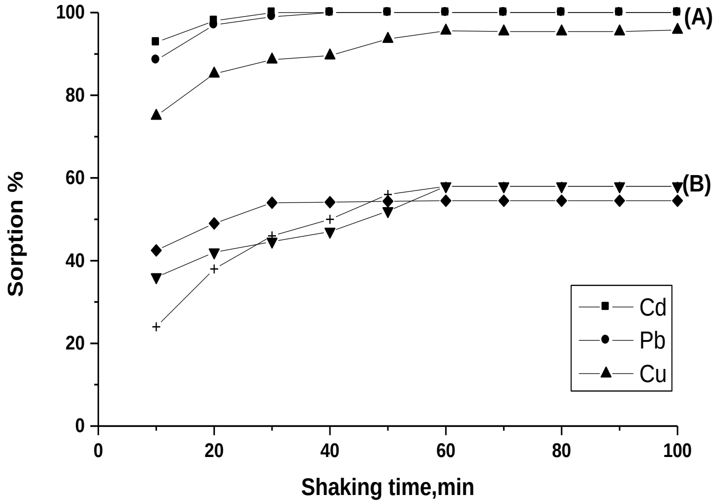

Figure 2. Effect of shaking time on the sorption of Cd^{2+}, Pb^{2+} and $Cu^{2+}$with (A) the modified SC-GNS and (B) the unmodified GNS.

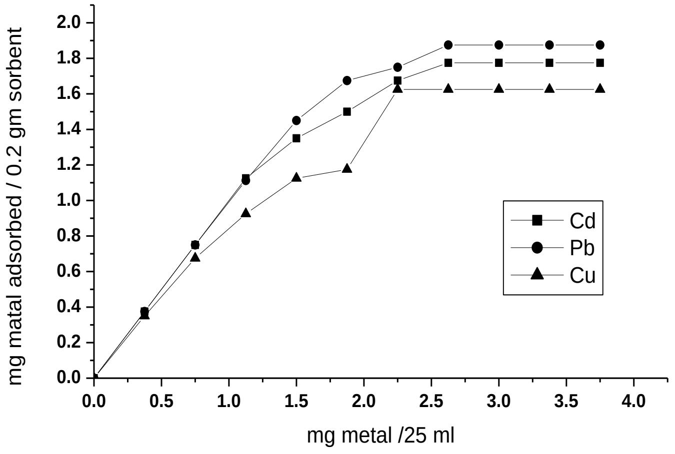

Figure 3. Extraction isotherm of Cd^{2+}, Pb^{2+} and $Cu^{2+}$with the modified SC-GNS.

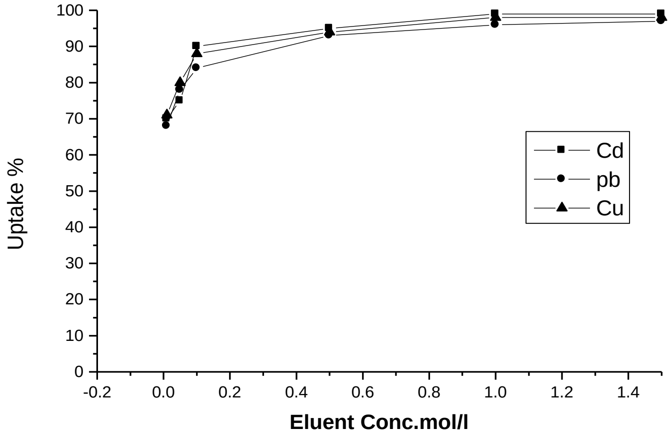

Figure 4. Effect of eluent concentration on the desorption with the modified SC-GNS

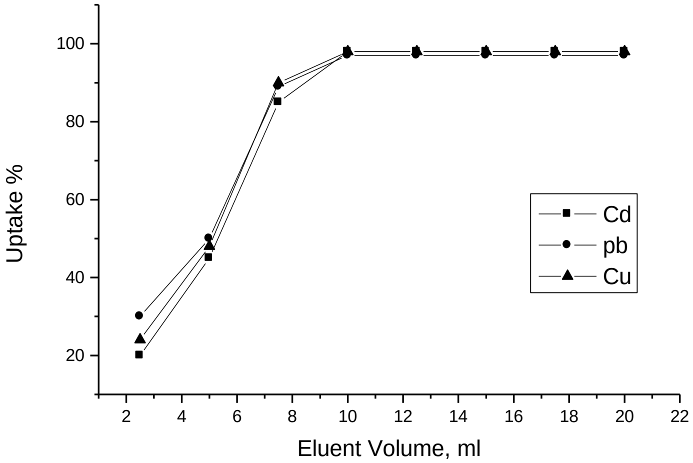

Figure 5. Effect of eluent volume on the desorption with the modified SC-GNS

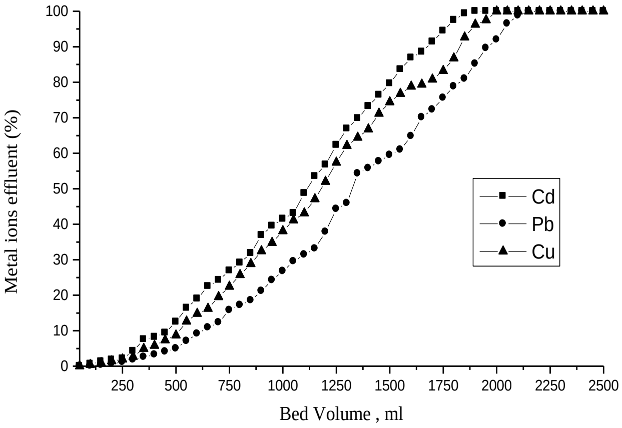

Figure 6. Breakthrough capacity of Cd^{2+}, Pb^{2+} and Cu^{2+} with the modified SC-GNS.

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

Parameters	**Metal ions**		
	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.Tolerance limits of some interfering ions.

Interfering ions	Tolerance limit (mg/l)		
	Cd^{2+}	Pb^{2+}	Cu^{2+}
Na^+	300	3000	600
K^+	500	1500	500
Ca^{2+}	250	500	350
Mg^{2+}	200	600	500
Cl^-	1000	3000	900
SO_4^{2-}	800	2000	900

Table 3.Preconcentration factor of the tested analyte on the modified SC-GNS

Metal ions	Initial volume mL	Final volume mL	Recovery %	CF[1]
Cd^{2+}	2000	10	96%	200
Pb^{2+}	2000	10	96%	200
Cu^{2+}	2000	10	95%	200

[1] CF: concentration factor

Table 4. Accuracy of modified SC-GNS sorbent, (n=5)

Metal ions	Added µg Concentration	Found µg (Mean ± S.D)	Recovery %	R.S.D%
Cd^{2+}	50	49.50±0.20	99	0.41
Pb^{2+}	50	49.25±0.42	98	0.85
Cu^{2+}	50	49.00±0.38	98	0.77

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

Sample	Metal ions	Without spiking	Spiked µg	Found µg (Mean ± S.D[2])	Recovery %	R.S.D%
Tap water	Cd^{2+}	ND[1]	50	49.9±0.99	99	2.0
	Pb^{2+}	ND[1]	50	51.0±0.99	102	1.9
	Cu^{2+}	5 µg	50	52.3±0.98	104	1.8
Intake of water treatment plant (New El-Azab)	Cd^{2+}	ND[1]	50	49.25±1.52	98	3.0
	Pb^{2+}	ND[1]	50	48.70±2.04	97	4.2
	Cu^{2+}	10 µg	50	58.00±1.72	96	2.9
Qaroun lake	Cd^{2+}	ND[1]	50	48.45±1.69	97	3.5
	Pb^{2+}	ND[1]	50	48.80±2.39	97	4.9
	Cu^{2+}	25 µg	50	73.90±2.95	98	4.0

[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 µg/l	Ref.
Ambersorb 563	Cd , Pb	8-10	0.25 $mol.L^{-1}$ HNO_3	5	125	0.33,72	**[27]**
Modified TA-GNS	Cd , Cu , Pb	6	1 $mol.L^{-1}$HCl	4	160	0.72,1.6,0.64	**[28]**
Amberlite XAD-4 Functionalized with 2-HydroxybenzaldehydeThiosemicarbazone	Cd ,Cu, Pb	6	2 $mol.L^{-1}$ HNO_3	1	100	0.95, 0.87, 1.09	**[29]**
N,N´-disalicylidene ethylene diamine -Modified Graphene	Cu	5.3	4$mol.L^{-1}HNO_3$	1	10	4.6	**[30]**
Modified SC-GNS	Cd , Cu , Pb	4-6	1 $mol.L^{-1}$HCl	4	200	0.28,1.2,0.48	**This work**

4. Comparison with other extractors.

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

5. Conclusions

The strategy for treating GNS as a biomass with the safe sodium carbonate in order to enhance the sorption capacity for Cd^{2+}, Pb^{2+} and Cu^{2+} was confirmed. The proposed analytical method for the determination, separation and preconcentration of the studied ions based on column packed with one gram modified SC-GNS prior FAAShas successfully been achieved as an alternative strategyfor other methods.

Finally we can conclude that, the modified SC-GNS is not only a simple and cheap natural extractor for cadmium, lead and copper with high sorption capacity, but also, sensitive and precise method for preconcentration the trace metal ions from water samples. The great advantage of this work is that, no need to use toxic reagents, especially carcinogenic reagents. Therefore, the new proposed method is very simple, ecofriendly to nature.

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