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Combination of solid-phase extraction and flame atomic absorption spectrometry for simultaneous preconcentration and determination of some heavy metals in real samples

Alireza Asghari[a,*], Hajar Farzinia[a], Maryam Rajabi[a], Mehrorang Ghaedi[b]

[a]*Department of Chemistry, Semnan University, Semnan 35195-363, Iran*
Fax: +98 231 3354110; email: aasghari@semnan.ac.ir
[b]*Department of Chemistry, Yasouj University, Yasouj, 75918-74831, Iran*

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ABSTRACT

A sensitive and simple method for the simultaneous preconcentration and extraction of trace amounts of Cd^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, and Pb^{2+} ions in some real samples without using organic solvent has been reported. The method is based on the adsorption of these metal ions on 4-(2-Pyridylazo) resorcinol (PAR) loaded on activated carbon (AC). The retained analytes on modified activated carbon were eluted using 3.0 mL of 3.0 mol L^{-1} nitric acid. The influences of the various analytical parameters including pH, amount of sorbent, sample volume, and eluent type on the recovery efficiencies were investigated. The experimental data were fitted to different conventional isotherm models including Langmuir and Freundlich isotherm. Generally, Langmuir model was found to represent the experimental isotherm data better than Freundlich model. The paper discusses the thermodynamic parameters of the adsorption (the Gibbs free energy, entropy, and enthalpy). Our results demonstrate that the adsorption process was spontaneous and exothermic. The effects of interference ions on retentions of the analytes were also examined. The recoveries of analytes were generally quantitative with a relatively low RSD. The method has been successfully applied for these metal ions content in some real samples.

Keywords: Heavy metal; 4-(2-Pyridylazo) resorcinol; Isotherm; Kinetic; Activated carbon; Solid-phase extraction; Atomic absorption spectrometry

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1. Introduction

The level of trace metal ions in various samples such as natural and wastewater, alloy, biological and food samples is extremely low. Due to the matrix effect, which invariably influences normal instrumental analysis, their direct determination with various instrumental methods is difficult [1–4]. In addition, some metal ions have low concentrations (near or below the limit of detection (LOD) of the instrument) and complicated matrices that these difficulties can be overcome via performing a prior preconcentration step and lead to simplified heavy metal determination [5].

Several methods of preconcentration include solvent extraction, [6,7] adsorption, [8] membrane extraction [9], coprecipitation [10–13], ion exchange [14,15],

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*Corresponding author.

and solid-phase extraction has been reported. Among them, solid-phase extraction (SPE) is preferred because of the fast, simple, and direct application in microliter volume without any sample loss, higher preconcentration factor, rapid phase separation, time and cost saving [16–29].

Activated carbon (AC) has been proven to be an effective adsorbent for the removal of wide variety of organic and inorganic pollutants [30–33] due to its large surface area, high adsorption capacity, porous structure, selective adsorption, and high purity [34–36]. However, without any surface treatment, activated carbon does not adsorb metal ions quantitatively at trace and ultra-trace levels [37,38], which prompts us to study the possibility of modifying traditional activated carbons with organics chelating agent to increase its adsorption tendency and capacity with respect to metal ions [39].

The purpose of this work is preconcentration and separation of Cd^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, and Pb^{2+} ions on activated carbon modified with 4-(2-pyridylazo) resorcinol (PAR) in some water and food samples. The analytical parameters for quantitative recoveries of analytes were investigated.

2. Experimental

2.1. Apparatus

The heavy metal ions were measured with a 680 AA atomic absorption spectrometer (Shimadzu, Japan) equipped with a hollow cathode lamp and a deuterium background corrector, at respective wavelengths using an air-acetylene flame. The instrumental parameters were those recommended by the manufacturer. A BEL PHS-3BW pH-meter (Italy) with a combined glass-Ag/AgCl electrode was used for adjustment of test solution pH. A UV–vis 1650 PC spectrophotometer (Shimadzu, Japan) was used to measure the absorbance of PAR solution. A peristaltic pump (Lambda, Switzerland) was used for controlling the flow rate of the solution in column process.

2.2. Reagents and solutions

Acids, bases, and the ligand 4-(2-pyridylazo) resorcinol (PAR) were of the highest purity available from Merck Company (Darmstadt, Germany) and were used as received. Doubly distilled water was used throughout. Analytical grade nitrate salts of cadmium, lead, nickel, copper, and cobalt (all from Merck) were of the highest purity available and used without any further purification. The pH of solution was adjusted via addition of dilute HCl and NaOH to acetate solution to prepare desired pH solution. Activated carbon (AC) [gas chromatographic grade, 40–60 mesh from Merck] was cleaned in hydrochloric acid for 2 days. Then, it was washed with water and dried at 110°C for 1 day.

2.3. Preparation of PAR-impregnated activated carbon

PAR-modified activated carbon (PAR-AC) was prepared by dissolving 48 mg of PAR in water to 0.4 g of AC in a beaker. After 3 h, the solutions were filtered through the filter paper and activated carbons were washed with distilled water. Finally, the mixtures were dried at 70°C overnight. The solid-phase columns were initially preconditioned by passing the blank solution with desired pH. A Teflon column (50 mm length and 7.0 mm inner diameter) equipped with glass wool plugs at the end of the column was filled up to a height of about 10 mm with PAR-AC.

2.4. Preconcentration procedure

The pH of solutions containing analyte ions was adjusted to 6.0. The sample solutions were passed through 0.4 g of AC-PAR at a flow rate of $2.5\,\mathrm{mL\,min^{-1}}$. The adsorbed ions were then eluted with 3.0 mL of $3.0\,\mathrm{mol\,L^{-1}}$ nitric acid in water with a flow rate of $3.0\,\mathrm{mL\,min^{-1}}$. The analyte ions in the eluent were determined by flame atomic absorption spectrometer.

2.5. Pretreatment of real samples

Dill and lettuce were purchased from Semnan Iran. Before the analysis, the samples were completely grilled and cut to tiny pieces and dried. 40.0 g of dill and lettuce were heated in silica crucible for 3 h on a hot plate, and the charred material was transferred to furnace for overnight heating at 650°C. The residue was cooled, treated with 10.0 mL concentrated nitric acid and 3.0 mL 30% H_2O_2 again kept in the furnace for 2 h at the same temperature so that no organic compound traces were left. The final residue was treated with 3.0 mL concentrated hydrochloric acid and 2–4 mL 70 (% W/V) perchloric acid and evaporated to fumes, so that all the metals were converted to their respective ionic analogs. The solid residue was dissolved in water, filtered and by keeping the pH at 6.0 made up to 250.0 mL by addition of diluted KOH, acetate buffer, and distilled water. Then, the preconcentration procedure given in the previous section was applied.

Water samples were collected from Odim spring, Ziyarat, Gorgan, Iran. The organic content of the water samples was oxidized in the presence of 1% H_2O_2 and an addition of concentrated nitric acid. After acidification to 1% with concentrated nitric acid, they were stored in polyethylene bottles. For the preconcentration procedure, pH of the 250.0 mL of water samples was adjusted to 6.0 by using acetate buffer and the sample passed through the column at flow rate of 2.5 mL min^{-1}. The analyte ions retained on PAR-modified AC were eluted with 3.0 mL of 3.0 mol L^{-1} HNO_3. The effluent was sent to flame atomic absorption spectrometry for evaluation of their metal content evaluation.

3. Results and discussion

For obtaining maximum and precise signal for evaluation of metal ion content, the effective parameters such as carbon capacity of the modified activated, time of PAR loading on AC, pH of sample solution, sample volume, condition (type and volume and the concentration) of eluent, flow rate of the sample solution through the column, and the effect of matrix should be studied.

First of all, the capacity of AC for PAR was investigated to find out how much ligand (mg) is needed for saturation of AC in modification process. For this purpose, 10–70 mg PAR was added into a series of 100.0 mL beakers and mixed with 0.5 g AC in water. After 24 h, the mixture was filtered, and the absorbance of the solution was measured spectrophotometrically to find the free PAR (unadsorbed). The results are shown in Fig. 1. The results showed that one gram of AC can adsorb more than 120.0 mg PAR.

The effect of time on the modification of AC was studied by treating 60.0 mg of PAR, 0.50 g AC for different time. The obtained results showed that maximum adsorption of PAR on the surface of AC takes place after 3 h (Fig. 2).

3.1. *Effect of pH of sample solution on metal ion recovery*

The pH of the solution has significant effect in adsorption of trace elements on the sorbent surfaces. The effect of pH on the preconcentration of metals on AC loaded with PAR was studied by determination of each element. Fifty micrograms (250 mL; 0.2 μg mL^{-1}) of each element was preconcentrated in the pH range of 2.0–8.0 (by addition of diluted NaOH or HCl) by introducing 0.4 g PAR-AC. The elution was performed with 3.0 mL of 3.0 mol L^{-1} HNO_3. The data corresponding to each element are shown in Fig. 3. The results showed that the highest metal recovery values were found at the pH 6.0, for all metal ions. So, the pH 6.0 was selected for simultaneous preconcentration and extraction of analytes.

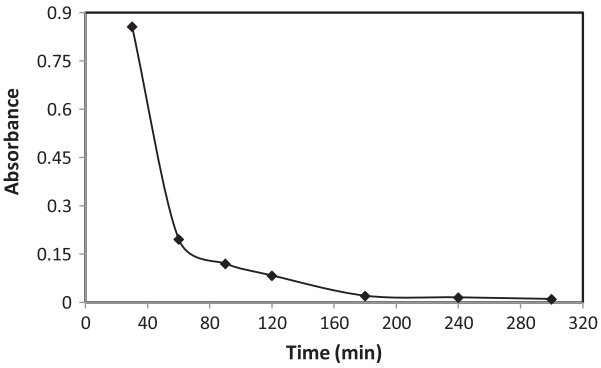

Fig. 2. Influence of time on the modification of activated carbon with PAR. Conditions: 500.0 mg activated carbon; 60.0 mg PAR, diluted to 100 mL.

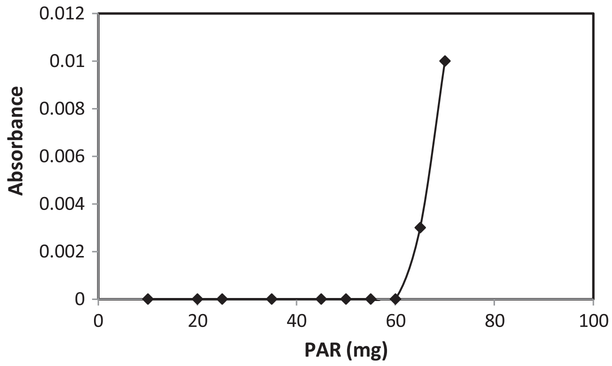

Fig. 1. The capacity of activated carbon for PAR. Conditions: 500.0 mg activated carbon; mixed well and stored for 24 h.

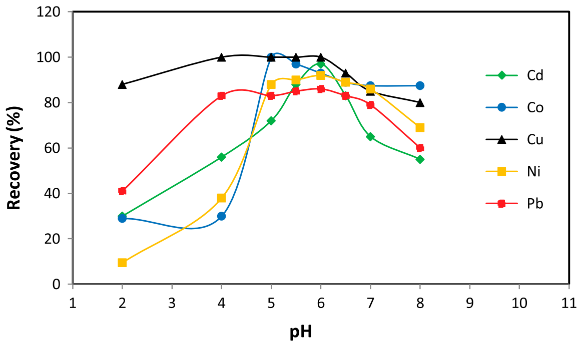

Fig. 3. Influence of pH on metal ion recoveries; sample flow rate, 2.5 mL min^{-1}; washing solution, 3.0 mL of 3.0 mol L^{-1} HNO_3.

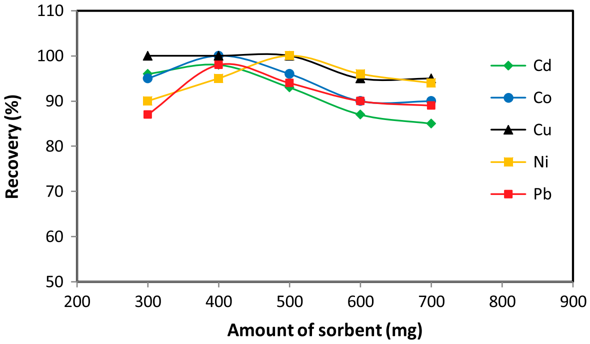

Fig. 4. Influence of amount of sorbent on adsorption of metal ions; washing solution, 3.0 mL of 3.0 mol L^{-1} HNO_3.

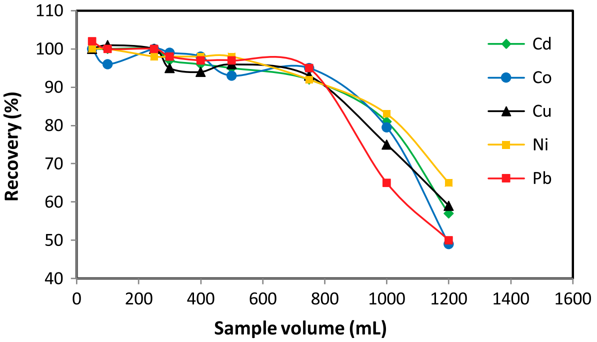

Fig. 5. Influence of sample volume on metal ion recoveries; sample flow rate, 2.5 mL min^{-1}; washing solution, 3.0 mL of 3.0 mol L^{-1} HNO_3,eluent flow rate, 3.0 mL min^{-1}.

3.2. Effect of amounts of sorbent

The influences of the amounts of PAR-AC filled to the column were also tested in range of 300–700 mg. The results are shown in Fig. 4. As can be seen in Fig. 4, the recovery can reach 95% by using 400 mg of sorbent. So, 400 mg of sorbent was selected for subsequent work. At the higher amounts of sorbent, the ion recoveries are reduced, probably due to the formation of charged species, therefore low tendency for sorption on solid phase (Fig. 5).

3.3. Selection of type, concentration, and volume of eluent

Desorption of the adsorbed materials on the solid phases is an important step for the solid-phase extraction studies. In this work, various eluting solution was used to identify the best eluent. A series of solvents such as HCl, H_2SO_4, H_3PO_4, and HNO_3 were used. The results are summarized in Table 1. The results show that the best recoveries were achieved by 3.0 mL of HNO_3 with the concentration of 3.0 mol L^{-1}. It was found that this solvent was sufficient to elute the metal ions from modified AC.

Table 1
Effect of eluting agent conditions on analytes recoveries

Eluent	Recovery (%)				
	Ni	Pb	Cu	Cd	Co
H_2SO_4, 5 mL, 3 mol L^{-1}	90.0	96.1	94.2	91.6	95.0
H_3PO_4, 5 mL, 3 mol L^{-1}	61.3	49.9	60.0	46.8	66.3
HCl, 5 mL, 3 mol L^{-1}	62.0	65.3	55.6	82.7	88.7
HNO_3, 5 mL, 3 mol L^{-1}	97.4	97.4	99.0	99.1	99.8
HNO_3, 5 mL, 1 mol L^{-1}	80.2	99.7	60.7	98	94.5
HNO_3, 5 mL, 2 mol L^{-1}	95.4	99.8	94.3	98.7	96.1
HNO_3, 5 mL, 5 mol L^{-1}	98.6	99.1	96.8	96.4	97
HNO_3, 3 mL, 3 mol L^{-1}	98.0	97.7	98.5	99.9	99.8
HNO_3, 4 mL, 3 mol L^{-1}	96.2	97.9	97.8	99.8	99.7
HNO_3, 7 mL, 3 mol L^{-1}	98.0	97.3	98.1	95.8	98.2

3.4. Effect of flow rates

The sample flow rate through the column is a very important parameter, since this is one of the steps that controls the time of analysis. Loading flow rate through the sorbent format should be fast enough to perform the solid-phase extraction in a short time, but it should be slow enough to allow the interaction between the metal complexes and the adsorbent packing material in the format .The influence of the sample loading rate on the analytical response was investigated between 1.0 and 5.0 mL min^{-1}. After sample loading, the column was rinsed with 10.0 mL water and the retained metal ions on sorbent were eluted with 3.0 mL of a 3.0 mol L^{-1} nitric acid at a flow rate of 3.0 mL min^{-1}. It was found that the flow rate in the range of 0.5–2.5 mL min^{-1} had no significant effect on the recoveries of the studied ions, and the optimal sample flow rate values were in the range between 1.0 and 2.5 mL min^{-1}. At flow rates higher than 2.5 mL min^{-1}, the response for Cd^{2+} and Cu^{2+} decreased. Considering these results, a sample flow rate of 2.5 mL min^{-1} was selected for further experiments. The influence of the eluent flow rate on the analytical response was also investigated between 1.0 and 5.0 mL min^{-1} under the optimum conditions. The results indicated that the analytes can be recovered quantitatively (above 95%) at flow rate 3.0 mL min^{-1}. Hence, all further studies were performed at the eluent flow rate of 3.0 mL min^{-1}.

3.5. Effect of sample volume

The volume of sample solution that can be subjected to the solid-phase extraction without reaching the breakthrough value is directly related to the

Table 2
Effects of interferences ions on the recoveries of the examined metal ions ($N = 3$)

Species	Tolerance limit				
	$W_{\text{ion}}/W_{\text{Cd}}$	$W_{\text{ion}}/W_{\text{Co}}$	$W_{\text{ion}}/W_{\text{Cu}}$	$W_{\text{ion}}/W_{\text{Ni}}$	$W_{\text{ion}}/W_{\text{Pb}}$
HCO_3^-, Na^+, K^+, NO_3^-, Mg^{2+}, Li^+, Ba^{2+}, Cr^{3+}, I^-	1,000	1,000	1,000	1,000	1,000
SO_4^{2-}	1,000	750	1,000	750	750
F^-	1,000	750	1,000	500	1,000
Cl^-	1,000	750	1,000	500	500
Ca^{2+}	750	1,000	750	1,000	750
Mn^{2+}	750	1,000	1,000	1,000	750
Fe	50	25	25	25	50
Sn^{2+}, Br^-	1,000	500	500	500	500
Ag^{2+}	1,000	1,000	500	1,000	500
Ni^{2+}	500	500	500	–	500
Cu^{2+}	500	500	–	500	500
Co^{2+}	500	–	500	500	500
Pb^{2+}	250	500	500	500	–
Cd^{2+}	–	500	500	500	500
Zn^{2+}	250	250	500	250	500

sorbent capacity. In order to obtain a higher enrichment factor, a large volume of sample solution is required. The influence of the sample solution volume on the metal sorption was studied by passing 50–1,200 mL volumes through the column at 2.5 mL min^{-1} flow rate. It was found that quantitative recoveries for all target analytes were obtained when sample volumes were less than 750 mL. Above this volume of sample solution, the recoveries decrease probably due to the excess analytes loaded over the column capacity. Hence, sample volume of 750 mL was selected for subsequent experiments. Thus, a preconcentration factor of 250 is achieved when 3.0 mL of HNO_3 is used to elute the adsorbed metals.

3.6. Effect of divers ions

To estimate the possible applications of the procedure for determination of these metal ions in real samples, the effect of foreign ions which interfere with the determination of heavy metal ions (at 0.2 mg L^{-1} level of the each heavy metal ion) was checked under the optimum conditions. Ions investigated by the presented method usually accompany analyte ions in various real samples. Tolerance limits of interfering ions were defined as the highest amount of foreign ions that produced an error not exceeding 5% in the determination of investigated analyte [28]. The obtained results are presented in Table 2. There are no interferences in the presence of large amounts of studied interfering ions, and this high selectivity enables the method for accurate and precise determination of Cd, Co, Cu, Ni, and Pb content in real samples.

3.7. Analytical performance

Under the optimum conditions, eight portions of standard solutions were treated and analyzed simultaneously by following the recommended procedure. LOD based on $3S_b/m$ definition (where m is slope of the calibration curve and S_b is the standard deviation for eight blank measurements), relative standard deviations (RSD) based on eight replicate measurements at 0.1 mg L^{-1} of the each heavy metal ions, linear range of the method, enhancement factors (calculated as the ratio of slopes of the preconcentration and direct calibration equations) [28], and enrichment factor were calculated. The results are listed in Table 3.

3.8. Applications and accuracy of method for real samples

In order to estimate the applicability of the method to real samples with different matrices containing varying amounts of a variety of diverse ions, the method was applied to the separation/preconcentration of metal ions from different matrices. Agricultural product such as dill and lettuce and spring water samples was used as real samples. The reliability and accuracy of method were tested by standard addition method [40]. The percent of recoveries and relative standard deviations for each element in spiked samples are summarized in Table 4. As could be seen,

Table 3
Specification of presented method at optimum conditions for each element

Parameters	Cd	Co	Cu	Ni	Pb
Linear range (ng mL^{-1})	5.0–150.0	15.0–1000.0	10.0–500.0	15.0–1000.0	20.0–1000.0
R^2	0.9966	0.9987	0.9991	0.9951	0.9989
Detection limit (ng mL^{-1})	1.47	4.45	2.92	4.51	6.15
RSD (%)	1.46	1.60	2.10	1.24	1.80
Preconcentration factor	250	250	250	250	250
Enhancement factor	76.3	30.6	45.1	45.1	67.2

Table 4
Levels of analyte ions in lettuce and dill samples ($N = 3$)

Ion	Added (μg g^{-1})	Found (μg g^{-1})	RSD	Recovery (%)
Lettuce				
Cd	0	12.8	1.5	–
	5	17.8	1.2	100.0
	10	22.6	1.0	98.0
Co	0	–	–	–
	5	5.1	1.9	102.0
	10	9.8	1.7	98.0
Cu	0	16.7	2.3	–
	5	21.6	2.0	98.0
	10	26.5	1.8	98.0
Ni	0	14.8	2.1	–
	5	19.6	1.9	96.0
	10	24.5	1.8	97.0
Pb	0	21.4	1.8	–
	5	26.3	1.9	98.0
	10	31.5	1.6	101.0
Dill				
Cd	0	1.7	2.7	–
	5	6.7	2.4	100.0
	10	11.5	2.5	98.0
Co	0	–	–	–
	5	5.1	2.0	102.0
	10	9.9	1.8	96.0
Cu	0	13.9	1.8	–
	5	19.0	1.5	102.0
	10	23.9	1.7	100.0
Ni	0	4.1	1.4	–
	5	9.3	1.1	104.0
	10	13.8	1.2	97.0
Pb	0	6.3	1.9	–
	5	11.2	1.5	98.0
	10	16.2	1.6	99.0

satisfactory results were obtained for the elements examined. These results confirm the validity of the proposed method for the preconcentration of the investigated ions (Table 5).

3.9. Adsorption isotherms

Equilibrium data, commonly known as sorption isotherms, are basic requirements for the design of adsorption system. These data provide information on the capacity of the sorbent. The capacity of the adsorbent is an important factor to determine how much sorbent is required to quantitatively adsorb a specific amount of metal ion from solution. [34] The adsorption capacity is the maximum metal quantity taken up by 0.5 g of solid phase and given by mg metal ion per gram modified solid phase. In order to determine this, 2–16 mg of analytes was loaded to the column containing 0.5 g of modified AC and recoveries were investigated. The solid-phase heavy metal concentrations, q_e, were determined for each heavy metal in mixture of them by analyzing the corresponding heavy metal concentration before and after the adsorption using the equation below:

$$q_e = \frac{C_0 - C_e}{M} \tag{1}$$

Table 5
Levels of analyte ions in spring water samples ($N = 3$)

Ion	Added (μg L^{-1})	Found (μg L^{-1})	RSD	Recovery (%)
Cd	0	–	–	–
	40	40.1	2.1	100.2
	80	77.0	1.9	96.2
Co	0	–	–	–
	40	39. 3	1.8	98.2
	80	77.5	2.0	96.9
Cu	0	2.7	2.3	–
	40	42.2	1.9	98.8
	80	82.1	2.1	99.2
Ni	0	3.0	1.9	–
	40	43.4	1.6	101.0
	80	81.9	1.7	98.6
Pb	0	–	–	–
	40	41.2	1.5	103.0
	80	81.5	1.7	101.9

where C_0 and C_e are the initial and equilibrium heavy metal concentrations in the solution ($\mathrm{mg\,L^{-1}}$), and M is the sorbent dosage ($\mathrm{g\,L^{-1}}$). Then, the sorption data have been subjected to different sorption isotherms, namely Langmuir and Freundlich, to determine the sorbent capacity for each metal.

The Langmuir adsorption isotherm is one of the most well known and applied adsorption isotherms and can be represented by the following equation [41]:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \tag{2}$$

Eq. (2) can be expressed in a linear form:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{K_L q_{\max}} \tag{3}$$

where q_e is the amount of metal adsorbed per unit weight of the modified AC ($\mathrm{mg\,g^{-1}}$) at equilibrium, C_e, the equilibrium concentration in the solution ($\mathrm{mg\,L^{-1}}$), $q_{\max}$, the maximum adsorption capacity ($\mathrm{mg\,g^{-1}}$), and K_L, the adsorption equilibrium constant ($\mathrm{L\,mg^{-1}}$). A plot of C_e/q_e vs. C_e shows linearity; hence, Langmuir constants $q_{\max}$ and K_L can be calculated from the slope and intercept of the plot, respectively.

The Freundlich isotherm model describes that the ratio of solute adsorbed on solid surface to the solute concentration is a function of the solution concentration. This model is an empirical model allowing for multilayer adsorption on sorbent. The model has the following form [42]:

$$q_e = K_f C_e^n \tag{4}$$

The linear form of Freundlich model can be expressed as Eq. (5):

$$\log q_e = \log K_f + n \log C_e \tag{5}$$

where K_f ($\mathrm{mg^{1-n} L^n\ g^{-1}}$) is the Freundlich constant, which represents the adsorption capacity when metal ion equilibrium concentration equals to 1, and n is the heterogeneity factor representing the deviation from linearity of adsorption and is also known as Freundlich coefficient. A plot of vs. shows linearity; therefore, Freundlich constants n and K_f can be calculated from the slope and intercept of the plot, respectively.

The calculated Langmuir and Freundlich parameters and regression coefficients are presented in Table 6. The validity of each isotherm model can be checked by the fitness of the straight line (R^2). Accordingly, and as shown in Table 6, the R^2 of the Langmuir isotherm was greater than that of the Freundlich isotherm for the adsorption of all investigated metal ions. This indicates that the adsorptions of metal ions on sorbent are better described by the Langmuir model than the Freundlich model. This in turn suggests that adsorption occurs as the monolayer ions adsorb onto the homogenous adsorbent surface.

3.10. Adsorption kinetics

The process of the mention metal ions adsorption from an aqueous phase by any adsorbent can be explained by using kinetic models and examining the rate controlling mechanism examining of the adsorption process such as chemical reaction, diffusion control, and mass transfer. The kinetic parameters are useful in predicting the adsorption rate which can be used as important information in designing and modeling of the adsorption operation. In order to investigation the adsorption kinetics, the batch method was applied. The sorption of metal ions was carried out by agitating 400 mg of modified AC suspended in 100 mL solution with 5.0 mg $\mathrm{L^{-1}}$ concentrations of Cd(II), Co (II), Cu(II), Ni(II), and Pb(II) with constant stirring at the optimum conditions. The preconcentration process was performed in the time range of 5–180 min. Then, the mixture was filtered, and C_e and q_t were calculated (Fig. 6). To examine the controlling mechanism

Table 6
Isotherm parameters of adsorption at optimum conditions

Ion	Langmuir, $\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{K_L q_{max}}$				Freundlich, $\log q_e = \log K_f + n \log C_e$			
	R^2	y	$q_{\max}$ ($\mathrm{mg\,g^{-1}}$)	K_L ($\mathrm{L\,mg^{-1}}$)	R^2	y	n	K_f
Cd	0.9889	3.64x − 1.10	0.28	3.32	0.8268	0.13x − 0.99	7.66	0.37
Co	0.9814	0.54x + 0.08	1.75	7.04	0.8868	1.20x + 1.07	0.83	2.92
Cu	0.9769	0.09x + 0.13	10.71	0.74	0.8474	1.64x + 0.69	0.61	1.99
Ni	0.9986	0.57x + 0.14	1.73	4.48	0.9608	0.06x + 0.37	2.38	1.45
Pb	0.9837	0.29x + 0.67	3.47	0.42	0.9766	0.43x + 0.11	15.31	1.11

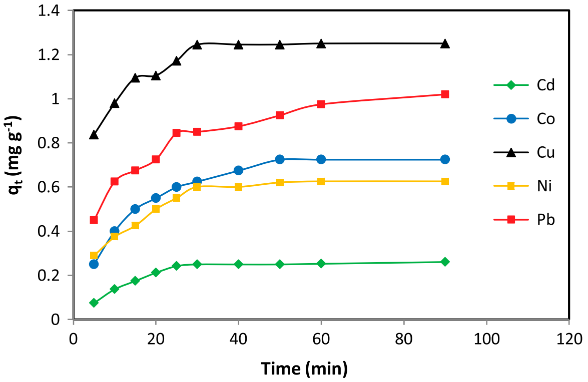

Fig. 6. Effect of contact time on the adsorption of metal ions onto the sorbent; initial concentration, 5.0 mg L^{-1}; 100 mL; 0.4 g sorbent, pH 6.0, 28 °C.

of the adsorption process, generally two kinetic models, namely pseudo-first-order and pseudo-second-order are used in literatures [43–45].

A simple kinetic analysis of adsorption is the pseudo-first-order kinetic model. The linear form of the pseudo-first-order equation given by Lagergren [36] Eq. (6):

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{6}$$

where q_e and q_t are the amounts of metal ions adsorbed (mg g^{-1}) at equilibrium time and at any instant of time, t, respectively, and k_1 (min^{-1}) is the rate constant of the pseudo-first-order adsorption operation. The straight line plots of (q_e–q_t) against t were used to determine the rate constant, k_1 (Table 7).

Table 7
Kinetic parameters of adsorption at optimum conditions

Ion	P-first-order $\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$			
	y	R^2	q_e (mg g^{-1})	k_1
Cd	−0.641x-0.31	0.9034	0.49	0.15
Co	−0.027x-0.21	0.9964	0.62	0.06
Cu	−0.026x-0.34	0.9228	0.45	0.06
Ni	−0.039x-0.26	0.9579	0.55	0.09
Pb	−0.016x-0.16	0.9778	0.69	0.04
Ion	P-second-order, $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t$			
	y	R^2	q_e (mg g^{-1})	k_2
Cd	3.24x + 40.2	0.9089	0.31	0.03
Co	1.13x + 13.7	0.9990	0.88	0.09
Cu	0.73x + 2.76	0.9945	1.37	0.19
Ni	1.28x + 13.3	0.9853	0.78	0.12
Pb	0.88x + 9.16	0.9973	1.32	0.08

The pseudo-second-order model, which has been popularly applied to adsorption systems, is expressed as follows [46]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{Q_e} t \tag{7}$$

where k_2 is the pseudo-second-order rate constant of adsorption (g mg^{-1} min^{-1}). The plot of t/q_t vs. t should give a linear relationship, which allows the computation of q_e and k_2 (Table 7).

As can be seen in Table 7, the R^2 of the pseudo-second-order model was greater than that of the pseudo-first-order one for the adsorption of all examined metal ions. Therefore, pseudo-second-order model is the more valid for the adsorption process than pseudo-first-order one.

3.11. Thermodynamic studies

Thermodynamic parameters related to the adsorption process, i.e. Gibb's free energy change (ΔG^0, kJ mol^{-1}), enthalpy change (ΔH^0, kJ mol^{-1}), and entropy change (ΔS^0, J mol^{-1}K^{-1}) are obtained from the experiments at various temperatures. At optimum

Table 8
Thermodynamic parameters of adsorption at optimum conditions

Ion	Parameters				
	ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})	T (^{0}K)	ΔG^0 (kJ mol^{-1})	K_c
Co	−12.80	−35.88	288.15	−2.75	3.16
			298.15	−1.86	2.12
			308.15	−1.48	1.78
			318.15	−1.07	1.50
Cd	−10.03	−27.90	288.15	−3.85	5.0
			298.15	−1.72	2.0
			308.15	−1.04	1.5
			318.15	−0.35	1.1
Cu	−35.53	−96.93	288.15	−7.61	24
			298.15	−6.82	15.66
			308.15	−5.62	9.0
			318.15	−4.38	5.25
Ni	−7.11	−18.40	288.15	−1.80	2.13
			298.15	−1.43	1.78
			308.15	−1.04	1.50
			318.15	−0.85	1.38
pb	−19.70	−57.86	288.15	−3.32	4.00
			298.15	−2.10	2.33
			308.15	−1.48	1.78
			318.15	−0.63	1.27

conditions, by mixing 400 mg of modified AC in 100 mL metal ion solutions with initial concentrations of 5.0 mg L^{-1}, the preconcentration procedures were carried out by batch method in a temperature-controllable water bath at 288.15, 298.15, 308.15, and 318.15 K.

The values of thermodynamic parameters for analyte adsorption on the sorbent can be determined from the temperature dependence. The values of ΔH^0 were calculated from the slopes and intercepts of linear regression of lnC_e vs. 1/T using the Clausius–Clapeyron equation (Eq. (8)):

$$in\, C_e q = \left(\frac{\Delta H_0}{RT}\right) + D \tag{8}$$

where ΔH^0 is standard enthalpy, T is the absolute temperature (K), R is the universal gas constant (J mol^{-1} K^{-1}), and D is the intercept of the plot of lnC_e vs. $1/T$. The other parameters (K_c, ΔS^0, ΔG^0) were calculated by using the following equations [47]:

$$K_c = \frac{C_{ad,eq}}{C_{eq}} \tag{9}$$

$$\Delta G^0 = RTlnK_c \tag{10}$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \tag{11}$$

where K_c is equilibrium constant of the adsorption, ΔG^0 is standard Gibbs free energy, ΔS^0 is standard entropy, $C_{ad,eq}$ is the concentration of metal ions on the adsorbent at equilibrium, and C_{eq} is the equilibrium concentration of metal ions in solution (mg L^{-1}). The results are reported in Table 8. As seen in Table 8, the negative values of ΔS^0 correspond to a decrease in the degree of freedom of the adsorbed species while

Table 9
Comparative data for SPE preconcentration procedures for analyte ions in conjugation with FAAS

Metal ion	Immobilized ligand	Solid-phase material	Sample volume (mL)	PF	LOD (ng mL^{-1})	Refs.
Cu, Ni, Cd, Zn	N-(2-aminoethyl) salicylaldimine	Silica gel	500	100	0.2, 0.3, 0.1, 0.1	[48]
Ag, Pb, Pd	DBzDA18C6	Octadecyl silica	1,000	110	1.8, 8.0, 4.2	[49]
Co, Cu, Cd, Pb, Mn, Ni	1-(2-thiazolylazo)-2-naphthol	Amberlite XAD-1,180 resin	250, 500, 500, 1,000, 1,500, 1,500	50, 100, 100, 200, 300, 300	3.6, 0.8, 0.3, 1.1, 0.1, 0.2	[50]
Pb	Dithizone	Graphen	250	125	0.61	[51]
Cu, Co, Cd, Ni, Zn, Pb	o-aminophenol	Amberlite XAD-2	1,000	50, 100, 50, 65, 40, 40	4.0, 5.0, 2.0, 7.5, 2.5, 25.0	[52]
Cu, Ni, Zn	D2EHPA-TOPO	MWCNT	250	25	50, 40, 60	[53]
Cu, Zn, Pb, Cd	NBNBAEED	MWCNT		80, 80, 20, 60	0.69, 0.48, 8.9, 0.25	[54]
Cd, Ni, Pb, Zn	4,4-IPBATP	MWCNT	1,750	178	1.6, 2.4, 5.6, 1.3	[55]
Cr, Cu, Ni	BHAPPDI	Diaion SP-850	1,250	125	6.2, 7.8, 5.2	[56]
Pb, Cu, Ni, Co, Cd	Aminothioamidoanthraquinone	Silica gel	25–100	–	22.5, 1.0, 2.9, 0.95, 1.1	[57]
Cu, Cd, Co, Pb, Zn, Mn	Quinalizarin	Amberlite XAD-2	1,000	100, 50, 40, 50, 100, 66	2.0, 1.3, 5.0, 15.0, 1.0, 1.6	[58]
Cd, Co, Cu, Ni, Pb	PAR	Activated carbon	750	250	1.47, 4.45, 2.92, 4.51, 6.15	Present work

Note: LOD: Limit of detection PF: Preconcentration factor EF: Enrichment factor DBzDA18C6: Dibenzyl diaza-18-crown-6 D2EHPA-TOPO: di-(2-ethyl hexyl phosphoric acid—tri-noctyl phosphine oxide MWCNT: Multiwalled carbon nanotube NBNBAEED: (E)-N1-(4-nitro-benzylidene)-N2-(2-((E)-4- nitrobenzylideneamino)ethyl) ethane-1,2-diamine 4,4-IPBATP: 4-(4-isopropylbenzylideneamino)thiophenol BHAPPDI: Bis(2-hydroxyacetophenone)-1,2-propanediimine the negative enthalpy changes (ΔH^0) indicate that adsorption followed exothermic processes. The negative values of ΔH^0 and the decrease in the absolute value of ΔG^0 with rise in temperature show that the sorption is favored at low temperature and the negative free energy values ΔG^0 indicate the feasibility of the process and its spontaneous nature without an induction period.

3.12. Comparison with other solid-phase extraction (SPE) methods

A comparison of the proposed method with other preconcentration procedures using various modified adsorbents is given in Table 9. Table 9 indicates the type of complexing agent, the type of adsorbent, sample volume, the preconcentration factor (PF), and the LOD of the various SPE procedures developed for metal ions determinations with FAAS. The PFs and LODs obtained were better or comparative with the other methods described in the literature.

4. Conclusions

A simultaneous preconcentration of Cd, Co, Cu, Ni, and Pb from aqueous solutions on an activated carbon impregnated with PAR column was successfully developed. The results presented have confirmed its applicability to the separation and preconcentration of these ion contents in low concentrations. The method is simple, accurate, and economical and can be applied for the determination of these heavy metal ions in environmental samples. The accuracy and precision of the proposed SPE method were reported in terms of recovery (%) ranging from 98 to 104% and R.S.D. (%) ranging from 1.1 to 2.7%.

The adsorption isotherm was obtained and the data in the linear form of Langmuir equation gave satisfactory correlation coefficients. The data indicated that the adsorption kinetics of metal ions on PAR-AC followed the pseudo-second order. The dependence of heavy metal ions adsorption on temperature was investigated, and thermodynamic parameters of adsorption (ΔH°, ΔS°, and ΔG) were calculated. The negative enthalpy changes (ΔH°) indicated that adsorption followed exothermic processes. The dependence of free energy change value on temperature showed that the adsorption process favored at high temperatures.

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Symbols

C_0 — initial concentration in the solution ($\mathrm{mg\,L^{-1}}$)
C_e — equilibrium concentration in the solution ($\mathrm{mg\,L^{-1}}$)
M — sorbent dosage ($\mathrm{g\,L^{-1}}$)
q_e — amount of metal adsorbed per unit weight of the modified activated carbon at equilibrium ($\mathrm{mg\,g^{-1}}$)
$q_{\max}$ — maximum adsorption capacity ($\mathrm{mg\,g^{-1}}$)
K_L — adsorption equilibrium constant ($\mathrm{L\,mg^{-1}}$).
K_f — Freundlich constant ($\mathrm{mg}^{1-n}\mathrm{L}^n\ \mathrm{g}^{-1}$)
q_t — amounts of metal ions adsorbed at equilibrium time ($\mathrm{mg\,g^{-1}}$)
k_1 — rate constant of the pseudo-first-order adsorption operation ($\mathrm{min^{-1}}$)
t — time of adsorption
k_2 — pseudo-second-order rate constant of the adsorption ($\mathrm{g\ mg^{-1}\ min^{-1}}$)
ΔG^0 — standard Gibbs free energy ($\mathrm{kJ\ mol^{-1}}$)
ΔH^0 — enthalpy change ($\mathrm{kJ\ mol^{-1}}$)
ΔS^0 — entropy change ($\mathrm{J\ mol^{-1}K^{-1}}$)
T — the absolute temperature (K)
K_c — equilibrium constant of the adsorption
$C_{\mathrm{ad,\ eq}}$ — concentration of metal ions on the adsorbent at equilibrium

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