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Microchemical Journal

Development of a fabric phase sorptive extraction method using ethylenediamine tetra-acetic acid modifier for quantitative determination and elimination of Pb^{2+}, Cu^{2+} and Zn^{2+} cations in real sample solutions

Mohsen Pouyan , Gholam Hossein Rounaghi [*] , Behjat Deiminiat

Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Mashhad, Iran

ARTICLE INFO

ABSTRACT

A novel and simple fabric phase sorptive extraction technique based on using ethylenediamine tetra-acetic acid (EDTA-FPSE), was used for selective solid phase extraction of Pb^{2+}, Cu^{2+} and Zn^{2+} cations followed by using inductively coupled plasma-optical emission spectrometry (ICP-OES). Then, the synthesized adsorbent was characterized by field emission scanning electron microscopy (FESEM) and energy dispersive X-Ray (EDX) analysis. The effect of some parameters including pH of the sample solution, extraction time, sample solution volume and the type and concentration of desorbent solution was investigated and they were optimized in details. Under the optimum experimental conditions, the limits of detection (LOD) were found to be: 0.062, 0.032 and 0.036 μg/L for Pb^{2+}, Cu^{2+} and Zn^{2+} cations, respectively and the limits of quantification (LOQ) were equal to 0.18, 0.1 and 0.12 μg/L for Pb^{2+}, Cu^{2+} and Zn^{2+} cations, correspondingly. Also, the reusability of the synthesized EDTA based on fabric phase sorptive adsorbent, showed that for these metal cations, it could be used for at least 12 adsorption/desorption cycles. Adsorption mechanism was evaluated by different isotherm models and based on the obtained results, the adsorption of Pb^{2+}, Cu^{2+} and Zn^{2+} cations is followed by Langmuir isotherm model with a maximum adsorption capacity of 92.60, 75.76 and 101.10 mg g^{-1} for Pb^{2+}, Cu^{2+} and Zn^{2+} cations, respectively. Finally, the selective behavior, high recovery percentage (more than 90 %), simple extraction procedure (easily separation of adsorbent from solution), makes the EDTA based on fabric phase sorptive extraction (EDTA-FPSE) technique as an unique technique for solid phase extraction of these heavy metal cations in different real sample solutions.

1. Introduction

Sample preparation, as one of the most important steps in quantitative measurements of the analytes in samples, has gained appreciable interests among analytical chemists in recent years [1,2]. The main purposes of this step are the reduction of the matrix effect and the separation of the target analytes from the sample solution in order to pre-concentrate and ready them for introduction into the analytical instruments [3]. Among different sample preparation techniques, solid–phase extraction (SPE) has been recognized as a promising alternative compared to the classical liquid–liquid extraction (LLE), which is undesirable due to the recent green analytical chemistry (GAC) regulations, regarding the high consumption of organic solvents [4]. However, Kabir and Furton, proposed a new green sample preparation technique in 2014 called fabric phase sorptive extraction (FPSE) [5]. This technique utilizes a natural or synthetic fabric as a substrate and an ultra-thin sorbent coating as the extraction medium. Unlike the substrates used in SPE and SPME, fabric substrates are not inert and play an essential role in determining the polarity and thus the selectivity of the extraction system [6].

A successful approach for preparation the inorganic polymers and organic–inorganic hybrid materials is being presented by the sol–gel technology [6]. Sol-gel technology has demonstrated numerous advantages, two of which are the compatibility of the technique with polymers and the polymerization processes [7] and the possibility to generate thermally and chemically-stable materials with controlled morphology, surface properties and pore structures [7]. Fabric phase sorptive extraction is the first sample preparation method that exploits the surface chemistry of the substrate. In fact, the selectivity and extraction efficiency of the FPSE, originate from the organic polymer, one or more

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organically modified inorganic precursor and the surface chemistry of the fabric substrate [6]. Moreover, due to the presence of active functional groups in fabric substrates, they can bond chemically to the sorbent coating in sol–gel network. As a result, FPSE offers a number of privileges over the other preconcentration techniques including: simplicity, low cost, minimal consumption of solvents, directly introducing the FPSE media into the vessel containing the sample matrix, minimization of sample preparation steps, reducing the potential sources of errors, using large number of organic ligands, sol–gel precursors and substrates and high analyte preconcentration factor in a very short period of time [6].

So far, FPSE technique has been used successfully for quantitative determination of different compounds in various media [8–13]. However, as far as we know, this method has only been utilized for the measurement of a few metal cations, which is probably due to the lack of selectivity and low extraction recovery. In addition, the chelating agent is added outside the FPSE medium and the prepared complex is extracted by the fabric sorbent and, therefore; the extraction process is a two-step process and sample loss is possible, which results in the decrease of the recovery and sensitivity [14–17]. Ethylenediamine Tetra-Acetic Acid (EDTA) has been used as a medication for management and treatment of heavy metal toxicity [18]. It has carboxylic acid groups in its structure which could be dissociated and interacted with heavy metals [19]. Since it is a unique reagent for interaction with heavy metal cations, our research aimed to apply FPSE technique merged using EDTA as a chelating agent. As far as we know, it is the first time for application of EDTA in FPSE technique for determination the concentration of Pb^{2+}, Cu^{2+} and Zn^{2+} cations in aqueous solutions.

Today, the widespread use of heavy metals causes to their leakage into the environment. Lead (Pb) is one of the most toxic heavy metals which has perfect industrial applications including manufacturing batteries, pigments, catalysis, alloys, etc. Long term exposure to Pb is accompanied with severe kidney damage and anemia [20]. Also, it has serious harmful effects on nervous system especially in children. According to the US agency, the maximum level of Pb^{2+} in human blood sample is 10 μg dl^{-1} [21]. Copper (Cu) is a heavy metal with widespread application. Although it is necessary for human health, since it is a cofactor of many redox enzymes; its high level causes to severe damage to liver and brain. Wilson's disease is a genetic disorder in which excess copper builds up in the body [22]. According to the World Health Organization (WHO), the concentrations of Cu^{2+} in drinking water ranges from ≤0.005 to >30 mg/l, primarily as a result of the corrosion of interior copper plumbing [23]. Zinc (Zn) is another heavy metal which is necessary for human health. It is a component of more than 300 enzymes which shows its vital role for human health [24]. In natural surface waters, the concentration of zinc is usually below 10 μg L^{-1}, and in ground waters, 10–40 μg L^{-1} [25]. Therefore, determination the accurate and precious level of the mentioned heavy metals in environmental and biological samples is highly recommended [26,27].

The synthesized adsorbent was characterized by the Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-Ray (EDX) analysis and used for selective solid phase extraction of Pb^{2+}, Cu^{2+} and Zn^{2+} metal cations. Then, the concentration of these metal cations, was determined by inductively coupled Plasma-Optical Emission Spectrometry (ICP-OES). The effect of different parameters affecting the extraction efficiency of the studied heavy metal cations, was studied in details and they were optimized. Also, different adsorption isotherm models were also investigated to understand the adsorption mechanism.

2. Experimental

2.1. Instruments

A BRNO-Mira3 LMU instrument (TESCAN, Czech Republic) was used for FE-SEM and EDX Analysis. The quantitative measurements were

Table 1
The operating parameters for the quantitative determination of the cations by ICP-OES.

RF power	1200 W
Plasma argon flow rate	15 L/min
Auxiliary argon flow rate	2.25 L/min
Nebulizer argon flow rate	0.65 L/min
Replicate measurements	3

performed with a sequential ICP spectrometer Varian Vista-MPX Simultaneous ICP-OES. The operating conditions of the ICP-OES equipment are presented in Table 1. Furthermore, a Metrohm 827 pH-meter (Switzerland) was used for the adjustment of pH. The most prominent atomic and ionic analytical spectral lines of the metal ions were selected for investigation, (Cu 324.754 nm, Pb 220.353 nm and Zn 213.856 nm).

2.2. Reagents

Lead nitrate ($Pb(NO_3)_2$, Merck, Germany), copper nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$, Merck, Germany) and zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, Merck, Germany) were used to make 1000 mg L^{-1} solutions of Pb^{2+}, Cu^{2+} and Zn^{2+} cations. Also, solutions of 0.1 mol/L HCl and NaOH were used for adjustment the pH of the solutions. The other material and reagents were purchased from Merck (Germany).

2.3. Surface cleaning and activation of fabric substrates

A 100 cm^2 segment of a cellulose fabric was cleaned with a copious amount of deionized water, followed by soaking in 1 M NaOH solution for 1 h. The base treated fabrics were then washed several times with deionized water, followed by treating with 0.1 M HCl solution for 1 h. The treated fabric was then washed with copious amount of deionized water and finally dried in ambient temperature. The dried fabric cellulose was stored in a clean airtight glass container until they were coated with the sorbents.

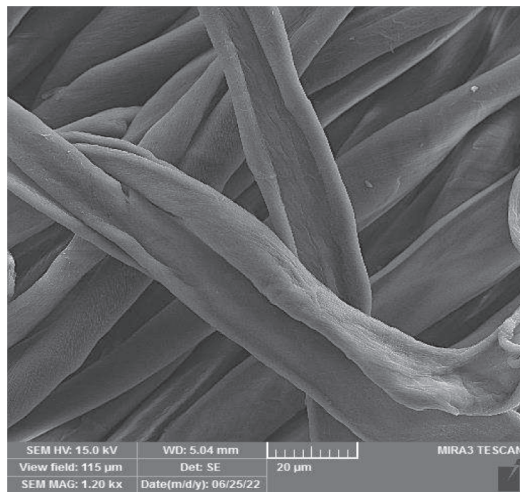### 2.4. Creation of EDTA based fabric phase sorptive adsorbent

A mixture containing 1 ml of tetraethoxysilane, 1 ml ethanol, 1 ml 0.1 mol/L EDTA prepared by using a 0.1 M phosphate buffer of pH 6.5 and 0.2 ml HCl and it was stirred well to obtain a sol solution [28]. A 2 × 2 cm^2 of fabric cellulose was immersed into the sol mixture for 45 min and then dried at room temperature for 24 h. Then, a polymer network containing EDTA molecules is formed. The resulting EDTA based fabric phase sportive adsorbent was used for solid phase extraction (SPE) of Pb^{2+}, Cu^{2+} and Zn^{2+} cations.

2.5. Analysis of real samples

Different water samples including Tap (Mashhad, Iran), River (Kashaf Rood, Mashhad, Iran) and drinking water (from a company in Mashhad, Iran) were filtered and after acidified with HNO_3 (pH adjusted to 2), stored in glass bottles at 4 °C. For the analysis of the studied heavy metals, appropriate amount of each water sample was subjected to the proposed analytical procedure.

2.6. EDTA-FPSE analytical procedure

50 ml of sample solution containing the target analytes were prepared at pH 4.5 using 0.1 mol/L buffer acetate and then the synthesized 2 × 2 cm^2 fabric adsorbent was added to the solution and stirred for 10 min at 400 rpm. After that, the adsorbent was removed from the solution and the adsorbed analytes eluted in 2 ml of 0.1 mol/L HCl and they were quantified by ICP-OES. The recovery percentage (RP) and adsorption capacity (q_e) were calculated according to Eqs. (1) and (2), respectively.
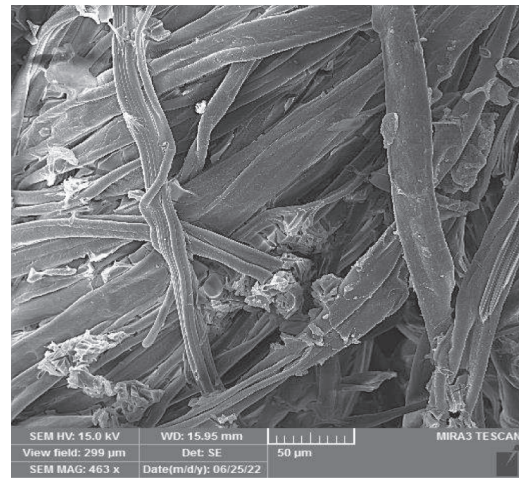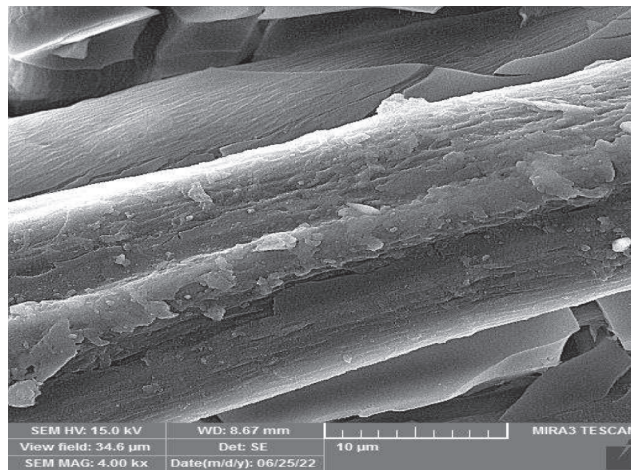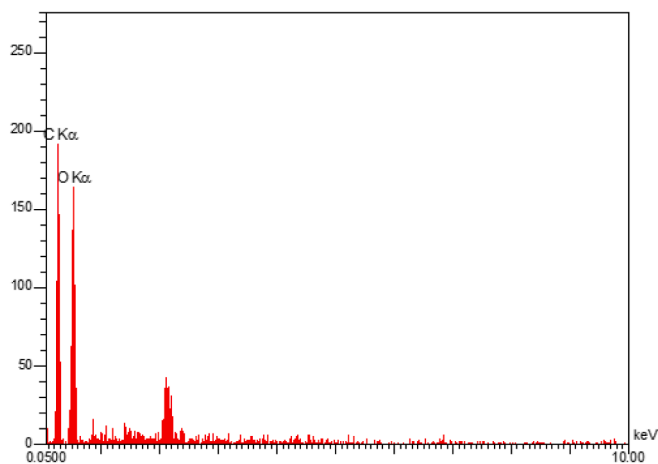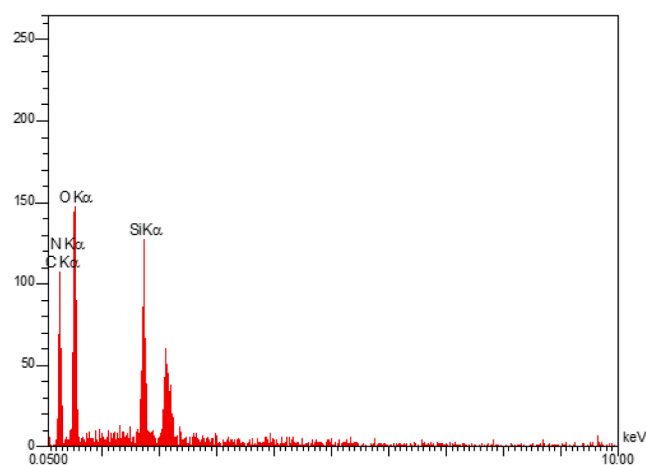
(a)
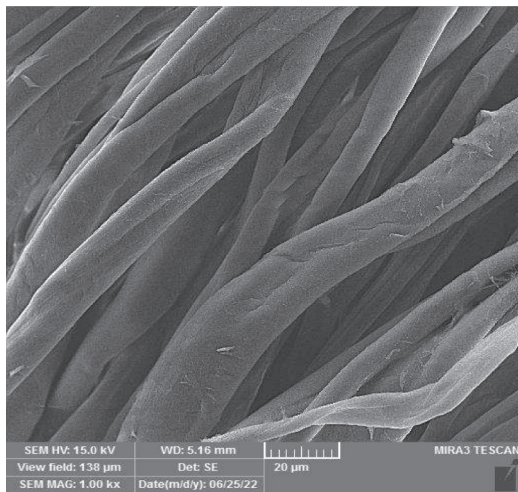
(b)
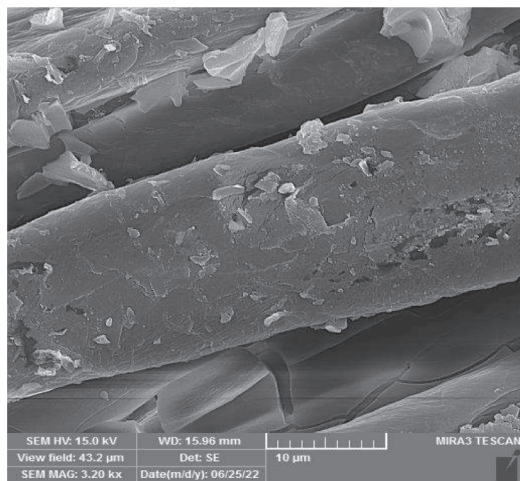
(c)

(d)

(e)

Fig. 1. FESEM images of the fabric substrate (a and b) and EDTA based fabric phase sorptive adsorbent (c–e).

(a)

(b)

Fig. 2. EDX analysis of fabric substrate (a) and EDTA based fabric phase sorptive adsorbent (b).

$$\text{RP} = \frac{C_F \times V_F}{C_0 \times V_0} \times 10 \tag{1}$$

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

In Eq. (1), C_F is the concentration of heavy metal cations in desorbent solution ($\mu g/L$), V_F is the desorbent solution volume (2 ml), C_0 is the initial concentration of analytes ($\mu g/L$) and V_0 is the volume of sample solution (50 ml). In Eq. (2), C_0 is the initial concentration of analytes (mg L^{-1}), C_e is the concentration of analytes after time t (mg L^{-1}), V is the volume of sample solution in L and m is the amounts of the adsorbent in g.

3. Results

3.1. Characterization of adsorbent

The synthesized adsorbent was characterized by FESEM and EDX analysis. The FESEM images of the fabric substrate and EDTA based fabric phase sorptive adsorbent, are presented in Fig. 1. According to Fig. 1a, and b, the fabric substrate has uniform smooth structure. However, after its modification to synthesize the EDTA based fabric phase sorptive adsorbent, the roughness of the surface changes as presented in Fig. 1c–e.
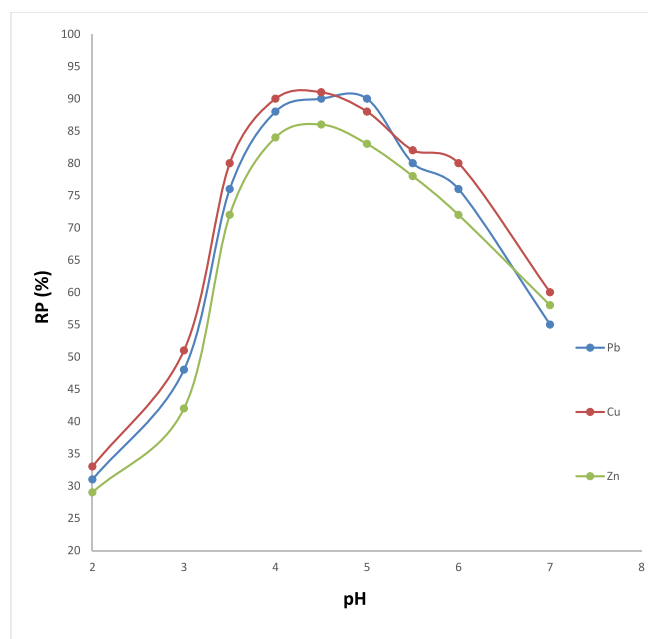

Fig. 3. Effect of pH of sample solution on the RP of the studied heavy metal cations. Conditions: 10 $\mu g/L$ Pb^{2+}, Cu^{2+} and Zn^{2+}, 5 min extraction time, 20 ml sample solution and 2×2 cm^2 fabric, 0.1 mol/L HCl as desorbent solution.

The EDX analysis was also performed on fabric substrate and EDTA based fabric phase sorptive adsorbent. Based on Fig. 2 which shows the EDX analysis of fabric substrate, its main elements are carbon and oxygen groups that are obviously presented at 0.28 and 0.52 eV, respectively. However, for EDTA based fabric phase sorptive adsorbent, the peaks of N and Si which are originate from EDTA and TEOS, are appeared at 0.39 and 1.7 eV, respectively, which show that the fabric substrate is modified successfully.

3.2. Effect of pH

For investigation the effect of sample solution pH on the RP of the studied heavy metal cations, this critical parameter was changed in the range of 2–7 and the obtained results are presented in Fig. 3. Based on the results, by increasing of pH value, the RP of the heavy metal cations increases and reaches to its maximum level at pH 4–5 for Cu^{2+},Pb^{2+} and Zn^{2+}cations. However, further increase in pH values causes to decrease of the RP of these heavy metal cations. Since the main mechanism for the adsorption of the heavy metal cations onto the adsorbent governed by: 1-Electrostatic interaction between positive charged cations and negative charged of carboxylic groups of EDTA in adsorbent, and 2-Ion-dipole interaction between the cation and O- and N- atoms of the adsorbent, therefore; it could be concluded that, at pH < 3, due to the protonation of O- and N- atoms and also incomplete dissociation of carboxylic acid groups of adsorbent, the RP of the heavy metal cations, decreases sharplly; however, in pH 4–5 due to the complete deprotonation of carboxylic acid groups and also deprotonation of N- and O-groups, the RP of the heavy metal cations increases and reaches to its maximum value [29]. Moreover, for further increase of pH value (pH > 5) the RP for Pb^{2+}, Cu^{2+} and Zn^{2+} decreases which could be attributed to the formation of metal hydroxides in solution. Therefore, for further experiments, pH 4.5 was selected as the optimum pH value for simultaneous solid phase extraction of Pb^{2+}, Cu^{2+} and Zn^{2+}cations.

3.3. Effect of extraction time

The effect of extraction time on the RP of Pb^{2+}, Cu^{2+} and Zn^{2+} cations, was studied in the time interval of 2–20 min. Based on the results
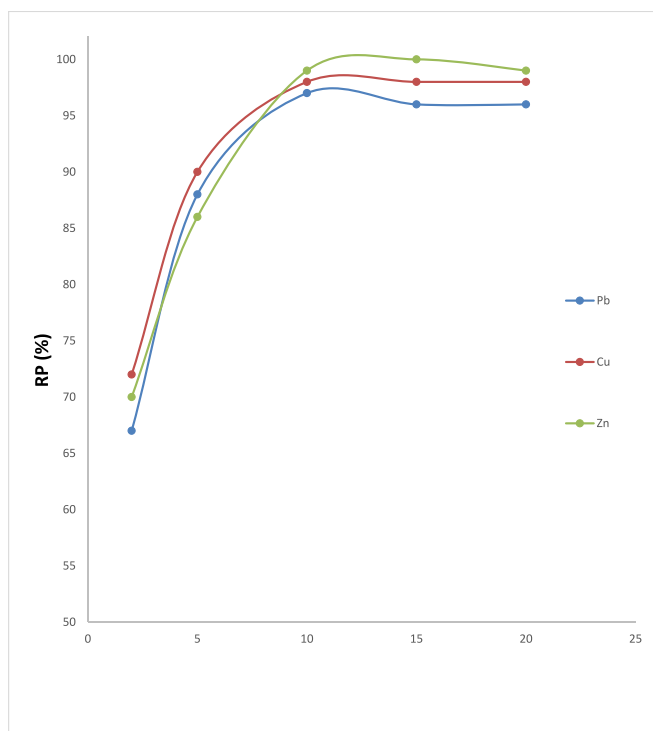
Fig. 4. Effect of extraction time on the RP of studied heavy metal cations. Conditions: 10 µg/L Pb^{2+}, Cu^{2+} and Zn^{2+}, pH 4.5, 20 ml sample solution and 2 × 2 cm^2 fabric, 0.1 mol/L HCl as desorbent solution.
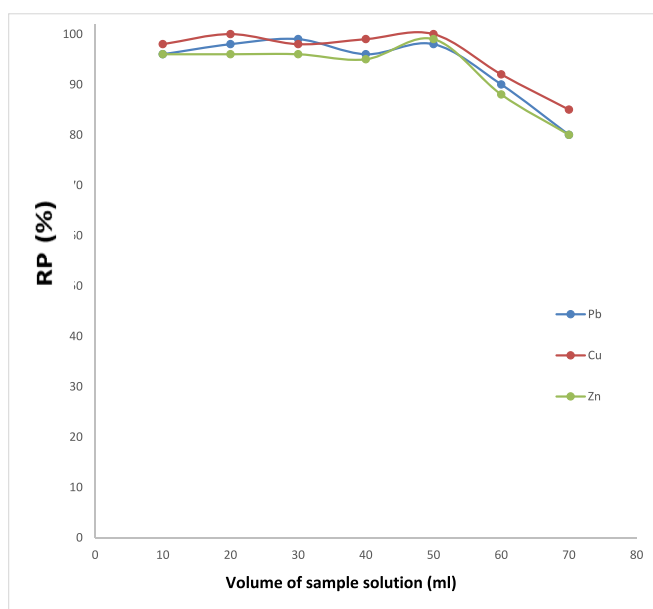
Fig. 5. Effect of volume of sample solution on the RP of Pb^{2+}, Cu^{2+} and Zn^{2+}cations. Conditions: 10 µg/L Pb^{2+}, Cu^{2+} and Zn^{2+}, pH 4.5, 10 min extraction time, 2 × 2 cm^2 fabric and 0.1 mol/L HCl as desorbent solution.

which are presented in Fig. 4, the maximum extraction time for Pb^{2+} and Cu^{2+} and Zn^{2+} was obtained after 10 min stirring of sample solution at 400 rpm. Therefore, 10 min extraction time was selected as the optimum extraction time for simultaneous solid phase extraction of Pb^{2+}, Cu^{2+} and Zn^{2+}metal cations.

3.4. Effect of sample solution volume

Since the adsorbent used in this study easily separated form sample solution, the effect of sample solution volume on the RP of Pb^{2+}, Cu^{2+} and Zn^{2+} cations was studied by testing different volumes of sample solution including 10, 20, 30, 40, 50, 60 and 70 ml. The obtained results are presented in Fig. 5. Based on the results, the maximum RP for Pb^{2+}, Cu^{2+} and Zn^{2+} cations was obtained for 10, 20, 30, 40 and 50 ml sample solution; however, for more volumes of sample solution, the RP of the studied metal cations decreased gradually which could be related to the limitation of available active sites of adsorbent for interaction by analyte ions at definite extraction time. Therefore, for further experiments, 50 ml of sample solution was selected as the optimum value.

3.5. Type and concentrations of desorbent solution

Different desorbent solutions with various concentrations were used for stripping of the heavy metal cations. The obtained results presented in Fig. 6, show that desorption is independent of the type of acid and depends on the acid concentration. 0.1 mol/L HCl and HNO$_3$ solution provides maximum desorption for the studied heavy metal ions from adsorbent. Therefore, in this research 0.1 mol/L HCl was used as an optimum desorption solution.

3.6. Effect of interfering ions

The effect of different interfering ions on the RP of Pb^{2+}, Cu^{2+} and Zn^{2+} cations (concentration of the Pb^{2+}, Cu^{2+} and Zn^{2+} cations is 20 µg/L) was studied by testing of various cations and anions as presented in Table 2. An ion is selected as interfere when it causes to change in the RP of an analyte in the range of ± 5 %. Based on the obtained results, the synthesized adsorbent showed a selective behavior toward Pb^{2+}, Cu^{2+} and Zn^{2+} metal cations in pH 4.5 which may be related to the presence of EDTA in the structure of the adsorbent.

3.7. Analytical figures of merit

Under the optimum experimental conditions, it was revealed that the proposed method has a linear range of 0.2–250 µg/L, 0.1–300 µg/L and 0.15–300 µg/L for Pb^{2+}, Cu^{2+} and Zn^{2+}, respectively. The calibration curve equations for Pb^{2+}, Cu^{2+} and Zn^{2+} are Y = 30.75C + 25.03, Y = 454.76C + 390.6 and Y = 128.95C + 166.9, respectively. The relative standard deviation (intra-day RSD) for seven replicate analysis of a solution containing 50 µg/L of Pb^{2+}, Cu^{2+} and Zn^{2+} are 5.9, 5.3 and 4.9 %. Also, the inter-day RSD values for five consecutive days are 5.8, 5.5 and 5.1 % for Pb^{2+}, Cu^{2+} and Zn^{2+}, respectively. The preconcentration factor was equal to 25 which could be calculated from division of initial sample solution volume (50 ml) to the volume of desorbent solution (2 ml). The limit of detection (LOD, 3Sb/m which Sb is the standard deviation of blank and m is the slope of calibration curve) were equal to 0.062, 0.032 and 0.036 µg/L for Pb^{2+}, Cu^{2+} and Zn^{2+}, respectively and the limit of quantification (LOQ, 10Sb/m) were equal to 0.18, 0.1 and 0.12 µg/L for Pb^{2+}, Cu^{2+} and Zn^{2+}, correspondingly.

3.8. Regeneration of adsorbent

One of the main strength of EDTA based on fabric phase sorptive adsorbent is its ability for separation from solution without centrifugation and loss of adsorbent. Therefore, it could be used for several adsorption/desorption cycles. The reusability of the synthesized EDTA based on fabric phase sorptive adsorbent was checked for 14 adsorption/desorption cycles and the obtained results are presented in Fig. 7. According to the obtained results, there is no significant changes after 12 adsorption/desorption cycles for the studied metal cations.
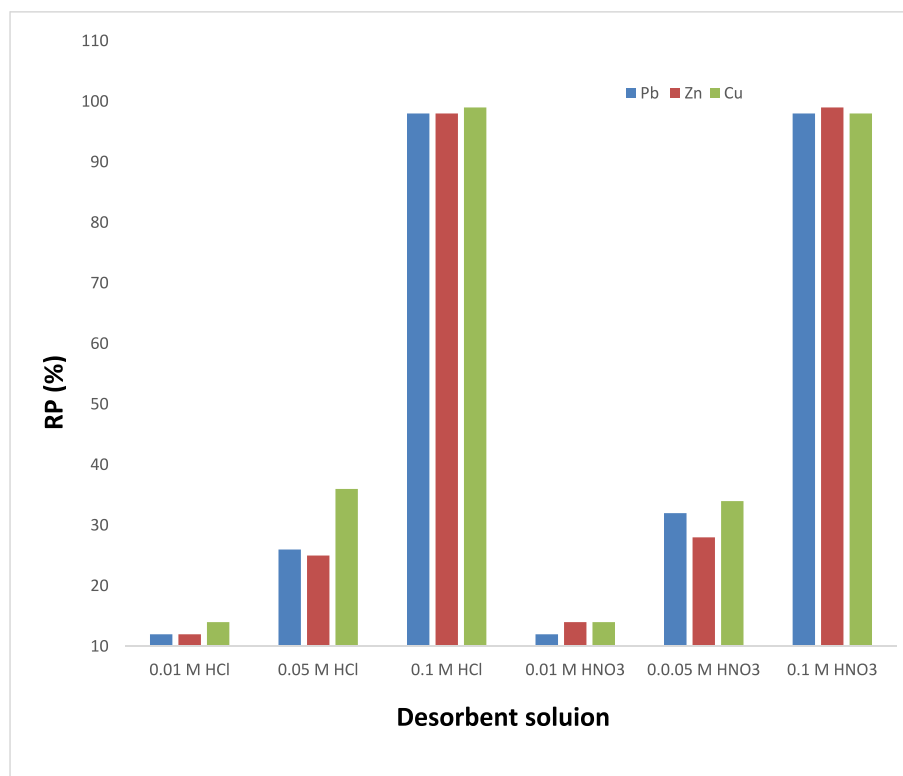
Fig. 6. Effect of type and concentration of desorbent solution on the RP of Pb^{2+}, Cu^{2+} and Zn^{2+} cations. Conditions: 10 µg/L Pb^{2+}, Cu^{2+} and Zn^{2+}, pH 4.5, 10 min extraction time.

Table 2
Effect of interfering ions on the RP of the studied heavy metal cations.

Ions	Added (µg L^{-1})	Pb^{2+} Recovery (%)	Zn^{2+} Recovery (%)	Cu^{2+} Recovery (%)
Na^+	50,000	98	98	97
K^+	50,000	97	96	96
Mg^{2+}	50,000	95	95	96
Ca^{2+}	50,000	96	96	96
Fe^{3+}	500	98	96	98
Cd^{2+}	100	99	96	99
Hg^{2+}	100	99	99	97
Co^{2+}	100	98	97	96
Ni^{2+}	100	99	96	95
NO^{3-}	100,000	94	96	95
SO_4^{2-}	100,000	95	96	95

3.9. Adsorption isotherm

3.9.1. Langmuir and Freundlich

To investigate the adsorption isotherm models, different concentrations of the analyte (Cu^{2+}, Zn^{2+} and Pb^{2+} in separate solutions) in the range of 10–150 mg L^{-1} were prepared and after adjusting at pH 4.5, fabric adsorbent (2×2 cm^2, 0.114 g) was added to the solutions and stirred for 30 min. Eq. (3), shows the Langmuir isotherm, relating to monolayer adsorption (q_{max} is a maximum adsorption capacity (mg g^{-1}) and K is a Langmuir constant (L mg^{-1})) [30]. The calculated q_{max} for Cu^{2+}, Pb^{2+} and Zn^{2+} are 75.76, 92.6 and 103.1 mg g^{-1}, respectively. Moreover, Freundlich isotherm (Eq. (4)), shows the multilayer adsorption of analyte (K_F (L g^{-1}) is a constant). The calculated Langmuir and Freundlich parameters for Cu^{2+}, Pb^{2+} and Zn^{2+} metal cations are provided in Tables 3–5. According to the results, the adsorption of the all analytes onto fabric adsorbent is a favorable process (n > 1). Also, since the R^2 values of Langmuir and Freundlich for Cu^{2+} and Pb^{2+} cations is higher than 0.95; it could be concluded that the adsorption of Cu^{2+} and

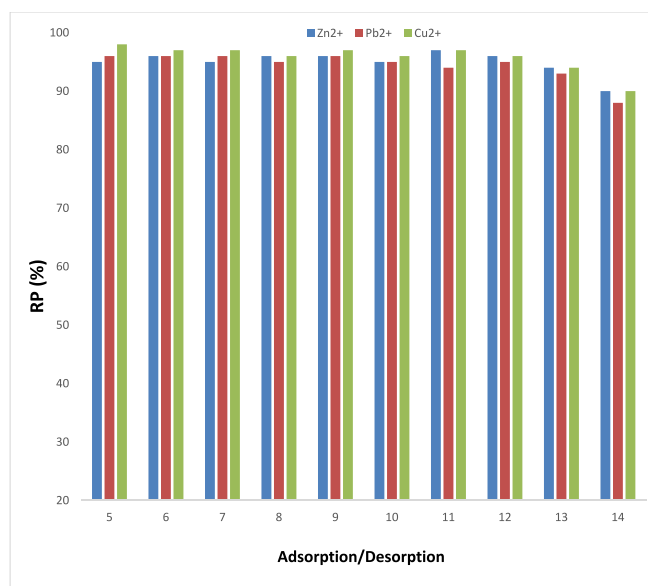**Fig. 7.** Effect of adsorption/desorption cycles on the RP of the studied heavy metal cations.

Pb^{2+} cations obeyed by both Langmuir and Freundlich isotherms. However, for Zn^{2+} its adsorption followed by the Langmuir isotherm (R^2 = 0.999 and 0.930 for Langmuir and Freundlich isotherms, respectively) [31].

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{K_{ads}}{q_{max}} \tag{3}$$

Table 3
Results of interpretation of isotherm models for Cu^{2+}.

Isotherm	Coefficients		
	q_{max} (mgg^{-1})	k_{ads} (Lg^{-1})	R^2
Langmuir Isotherm	75.76	10.06	0.993
Freundlich Isotherm	N	k_F	R^2
	1.50	6.83	0.981
Temkin Isotherm	b(kJ/mol)	A (Lmg^{-1})	R^2
	0.137	0.84	0.924

Table 4
Results of interpretation of isotherm models for Pb^{2+}.

Isotherm	Coefficients		
	q_{max} (mgg^{-1})	k_{ads} (Lg^{-1})	R^2
Langmuir Isotherm	92.60	14.12	0.997
Freundlich Isotherm	N	k_F	R^2
	1.99	10.39	0.980
Temkin Isotherm	b(kJ/mol)	A (Lmg^{-1})	R^2
	0.070	6.59	0.995

Table 5
Results of interpretation of isotherm models for Zn^{2+}.

Isotherm	Coefficients		
	q_{max} (mgg^{-1})	k_{ads} (Lg^{-1})	R^2
Langmuir Isotherm	103.10	9.13	0.999
Freundlich Isotherm	n	k_F	R^2
	2.11	10.26	0.930
Temkin Isotherm	b(kJ/mol)	A (Lmg^{-1})	R^2
	0.173	0.75	0.990

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

3.9.2. Temkin isotherm

Eq. (5), shows the formula of Temkin isotherm where A is an equilibrium binding factor (L/g) and $\beta = RT/b$ (b: heat of sorption coefficient). A and β provide from qe vs Ln Ce. According to the b values for Cu^{2+}, Pb^{2+} and Zn^{2+} cations which are presented in Table 3 (b < 8 kJ/mol), the adsorption of the heavy metal cations is a physical process [32,33].

$$q_e = \beta \, Ln \, A + \beta \, Ln \, C_e \tag{5}$$

3.10. Real samples

The proposed method was applied for determination the concentration of Cu^{2+}, Zn^{2+} and Pb^{2+} cations in different water samples. The obtained results are presented in Table 6. Based on the obtained results, the proposed method could effectively use for determination of trace levels of the studied heavy metal cations in different water samples (RP in the range of 98.1–103.4 for Pb^{2+}, 96.8–102.9 for Cu^{2+} and 98.4–103.5 for Zn^{2+}).

3.11. Comparison with other methods

The comparison of the proposed EDTA-FPSE technique with other preconcentartion procedures was performed and the results are presented in Table 7. Based on the results, low LOD values for the studied heavy metals, acceptable RSD, green view, rapidity (10 min extraction time), simplicity and reusability (12 adsorption/desorption cycles) of adsorbent makes EDTA-FPSE technique as a unique adsorbent for simultaneous SPE of Cu^{2+}, Zn^{2+} and Pb^{2+}.

4. Conclusion

In this research work, a novel sample preparation EDTA-FPSE technique was developed for selective determination of Pb^{2+}, Cu^{2+} and Zn^{2+} metal cations and their elemination by using ICP-OES. By optimizing the important parameters, it was revealed that pH 4.5 and 10 min extraction time provide maximum RP for these cations. Also, the synthesized adsorbent shows a selective behavior toward Pb^{2+}, Cu^{2+} and Zn^{2+} cations which may be attributed to the higher affinity of EDTA for the interaction with the studied heavy metal ions in this pH value. The combination of the fabric phase sorptive extraction technique and EDTA has been overcome the main shortcoming of the conventional FPSE method which has a low selectivity toward metal cations. Also, EDTA-FPSE can be used for other metal cations in case of pH optimization. By interpreting of the adsorption isotherm models, it was revealed that the adsorption of Pb^{2+}, Cu^{2+} and Zn^{2+} cations onto the adsorbent is followed by the Langmuir model with a maximum adsorption capacity of 92.60, 75.76 and 101.10 mg g^{-1} for Pb^{2+}, Cu^{2+} and Zn^{2+} cations, respectively. All in all, green aspect, high RP percentage, ease of operation and also the selective behavior, show that the EDTA based on fabric phase sorptive extraction (EDTA-FPSE) technique as a powerful sample preparation technique for quantitative determination and elemination of the heavy metal cations in different real sample solution.

Table 6
Results for determination the concentration of the studied heavy metal cations in different water samples. Results: Mean ± intra-day SD for three replicate analysis (SD in inter-day analysis).

Sample	Added (μgL^{-1})	Pb^{2+}		Cu^{2+}		Zn^{2+}	
		Founded (μgL^{-1})	Re (%)	Founded (μgL^{-1})	Re (%)	Founded (μgL^{-1})	Re (%)
Tap water	0	ND	–	2.10 ± 0.20(0.2)	–	30.0 ± 2.1(2.7)	–
	5.0	5.10 ± 0.20(0.3)	102.0	6.95 ± 0.30(0.6)	97.9	35.2 ± 2.0(3.1)	100.6
	10.0	9.81 ± 0.30(0.5)	98.1	12.30 ± 0.80(1.1)	101.6	41.0 ± 1.9(2.2)	102.5
Drinking water	0	ND	–	15.70 ± 1.0(1.4)	–	8.1 ± 0.7(0.9)	–
	5.0	5.15 ± 0.30(0.5)	103.0	20.70 ± 1.10(1.3)	100.0	13.0 ± 1.0(1.3)	99.2
	10.0	10.15 ± 0.60(0.9)	101.5	25.50 ± 1.0(1.4)	99.0	18.50 ± 1.0(1.1)	102.2
River water	0	3.80 ± 0.20(0.5)	–	10.50 ± 1.0(1.3)	–	21.0 ± 1.0 (1.2)	–
	5.0	9.10 ± 0.60(0.8)	103.4	15.0 ± 1.0(1.2)	96.8	25.90 ± 1.0(1.0)	99.6
	10.0	13.60 ± 0.90(1.0)	98.6	20.1 ± 1.0(1.1)	98.0	30.5 ± 1.0(1.0)	98.4

Table 7
Comparison of the proposed method with other reported method for solid phase extraction of the studied heavy metals.

Solid phase extraction	Linear range (µg/L)	RSD	LOD (µg/L)	References
Magnetic mesoporous carbon (Fe3O4@C, MMC)-FAAS		≤ 3.2 %.	2.8 for Pb^{2+} 0.87 for Cu^{2+}	[34]
silica coated magnetic multiwalled carbon nanotubes impregnated with 1-(2-pyridylazo)-2-naphthol-FAAS	–	≤ 3.3 %.	1.76 for Pb^{2+}	[35]
Magnetic graphene oxide nanocomposite-ICP-MS	1.0–150 for Pb^{2+} and Cu^{2+}	2.0–6.1 % Pb^{2+}, 0.8–6.0 % for Cu^{2+}	0.157 for Pb^{2+} 0.395 for Cu^{2+}	[36]
Magnetic Fe3O4 Alnus glutinosa Sawdust Biochar/SiO2/CTAB-FAAS	100–5000 for Pb^{2+} and Cu^{2+}	3.1 % Pb^{2+}, 1.1 % Cu^{2+}	1.55 for Pb^{2+} 0.24 for Cu^{2+}	[37]
Hydroxyapatite nanorods originated from eggshell-FAAS	Up to 400 µgL^{-1} Pb^{2+} Up to250 µg L^{-1} Cu^{2+} Up to 300 µg/L Zn^{2+}	2.2–2.7 % Pb^{2+}, 1.8–2.4 % for Cu^{2+}, 1.4–2.0 % for Zn^{2+}	5.12 for Pb^{2+} 0.72 for Cu^{2+} 0.55 for Zn^{2+}	[38]
Magnetic multi-walled carbon nanotubes (MMWCNT)-ICP-MS	0.1–50 µgL^{-1} Pb^{2+} 0.1–50 µg/L Cu^{2+}	1.5 % Pb^{2+}, 1.9 %for Cu^{2+}	0.011 for Pb^{2+} 0.009 for Cu^{2}	[39]
EDTA-FPSE-ICP-OES	0.2–250 µgL^{-1} Pb^{2+} 0.1–300 µg/L Cu^{2+} 0.15–300 µg/L Zn^{2+}	5.9 % Pb^{2+}, 5.3 % Cu^{2+}, 4.9 % Zn^{2+}	0.062 for Pb^{2+} 0.032 for Cu^{2+} 0.036 for Zn^{2+}	The present work

CRediT authorship contribution statement

Mohsen Pouyan: Writing – original draft, Investigation, Formal analysis, Data curation, Conceptualization. **Gholam Hossein Rounaghi:** Writing – review & editing, Validation, Supervision, Resources, Funding acquisition. **Behjat Deiminiat:** Writing – review & editing, Validation, Investigation, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

Acknowledgement

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