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Simultaneous application of cloud point and solid-phase extraction for determination of Fe(III) and Cu(II) ions by using SnO_2 nanopowder in micellar medium

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ABSTRACT

A new approach was developed for sensitive determination of Fe(III) and Cu(II) ions using SnO_2 nanopowder in the micellar medium on the contrary conventional cloud point extraction studies. The presented method contains a combination of solid-phase extraction and cloud point extraction. According to this procedure, the metal ions were firstly retained on modified SnO_2 nanopowder and then passed to the surfactant-rich phase. The effect of experimental variables including pH, concentration of reagents, eluting solution, incubation time, equilibration temperature, sample volume, and effects of interfering ions have been investigated and optimized systematically. The calibration graphs were linear in the range of 0.23–100.00 $\mu g\ L^{-1}$ and 0.30–110.00 $\mu g\ L^{-1}$ for Fe(III) and Cu(II), respectively. Under optimized conditions, the limits of detections were 0.07 and 0.09 $\mu g\ L^{-1}$ for Fe(III) and 0.09 $\mu g\ L^{-1}$ for Cu(II). The proposed method offers satisfactory analytical features by means of combining two different and efficient preconcentration techniques. In addition, the method can be evaluated as an alternative and fast method according to only-surfactant-mediated extractions. The validation of method was carried out by recovery tests and certified reference material (CRM) analysis. The acceptable and compatible results were obtained in the analysis of CRM and real samples.

Keywords: Solid-phase extraction; Cloud point extraction; Fe(III); Cu(II); SnO_2 nanopowder; Water samples; Flame atomic absorption spectrometry

1. Introduction

Trace metals play an important role for living metabolism, and their excess or deficiency can lead to biological disorder [1]. The determination of heavy metals in the environmental samples attracts great attention due to their dangerous effects on the ecosystem and human health. Copper as one of the heavy metals is an important nutrient at trace levels for life, but on the other hand, it is highly toxic for organisms such as algae, fungi, and many bacteria or viruses. Copper is also suspected as a reason for infant liver damages [2]. Among biologically important transition metal ions, iron plays a crucial role in many biological

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and environmental processes. Both Fe(III) deficiency and overloading induce serious disorders such as Huntington [3].

The use of surfactants in analytical chemistry has provided many new possibilities separation/preconcentration based on cloud point extraction (CPE) which is emerging as an important practical technique. The CPE as solvent-free and non-polluting method has been applied to separation and preconcentration of environmental and biological samples with a complicated matrix [4].

Solid-phase extraction (SPE) is one of the most employed preconcentration methods that can be applied in off-line or online systems with the advantage of possible automation. SPE consists of the retention of metal species (or derivatives) on the appropriate solid sorbent and the later desorption with the adequate solvent. Thus, the concentration and separation of the analyte from the rest of sample matrix is achieved [5]. SPE is preferred due to flexibility, absence of emulsion, simplicity, sampling in the field, and safety. SPE techniques require an adsorbent having selective adsorption ability [6].

Tin oxide (SnO_2) is an important material owing to useful properties such as transparency in the visible spectrum, strong physical and chemical interaction with adsorbed species, low operating temperature, and strong thermal stability in air (up to 500˚C) [7,8].

In recent years, nanostructure materials have attracted great attention in many fields [9–31]. The main purpose of this study was to develop a simple, sensitive, and accurate method for analysis of Cu(II) and Fe(III) species in real samples. A new method for sensitive determination of target metals was developed in combination with SPE and CPE using flame atomic absorption spectrometry (FAAS).

2. Experimental

2.1. Instrumentation

A Metrohm pH-meter (model 691, Switzerland) was used in order to adjust the pH at desirable values. A Chemtech Analytical Instrument model CTA-3000 atomic absorption spectrometer (Bedford, England) equipped with a flame burner was used for analysis of the metal ions. The instrumental parameters including lamp currents and wavelength were used as recommended by the manufacturer. Both metals were measured under optimized operating conditions by FAAS with an air–acetylene flame. A thermostatic water bath (Jeotech, Korea) was used to keep the temperature constant. A centrifuge (Hettich, Universal 120, England) was used for complete phase separation. A magnetic stirrer (Jeotech, Korea) was used for all steps in experiments.

2.2. Standard solutions and reagents

Analytical reagent-grade chemicals were used in this work. All plastic materials and glassware were cleaned by soaking in 10% HNO_3 solution and then rinsed with distilled water prior to use. Standard solutions (1,000 mg L^{-1}) of Fe(III) and Cu(II) ions were prepared from high-purity compounds supplied by Merck (Darmstadt, Germany). Amaranth (Aldrich) was used without further purification. 4.0 (v/v) % solution of Triton X-114 was prepared by diluting 4 mL of surfactant to 100 mL by water. A stock solution of 0.1 mol L^{-1} Na_2SO_4 was obtained by dissolving appropriate amount salt in 100 mL water. The working standard solutions were prepared by diluting stock standard solution. Britton–Robinson buffer solution in the pH range of 1–9 was used to adjust pH values. SnO_2 nanopowder was purchased from Aldrich, Germany.

2.3. Recommended procedure

Experimental procedures can be summarized in two steps. In the first step, 20 mg of Amaranth was dissolved in 12 mL distilled water and heated up to 40˚C for 35 min. Then, 7 mg of SnO_2 powder was added into the container, and the mixture was leaved at room temperature for 24 h. End of this process was obtained SnO_2 nanomaterial as modified with Amaranth.

In the second step, 1 mL of 4% Triton X-114, 3 mL of 0.1 mol L^{-1} Na_2SO_4, 1.5 mL of pH 6.0 buffer, 5 mL of sample solution including analyte ions (in the range of 0.23–100 μg L^{-1} for Cu(II) and 0.30–110 μg L^{-1} for Fe(III)), and 7 mg of modified adsorbent were mixed in a conical tube. After that, the mixture was stirred for 10 min in order to get suspension of nanopowder and was kept in a thermostatic bath at 45˚C for 5 min. Afterward, the aqueous and the surfactant-rich phase were separated by means of centrifugation at 3,500 rpm for 8 min. Subsequently, the SnO_2 nanopowder including analyte ions was settled down in the surfactant-rich phase. The contents of tube were cooled in an ice-bath; the surfactant-rich phase became viscous, and the upper aqueous phase was separated by a simple decantation. The surfactant-rich phase including metal complexes was treated with 2 mL of 0.8 mol L^{-1} HNO_3, and then a second round of CPE was applied to the solution in a thermostatic bath at 45˚C for 5 min. After phases were separated again by centrifugation for 8 min at 3,500 rpm, 200 µL of 2.0 mol L^{-1} HNO_3 was added to the solution for desorption of the analyte ions. Concentrations of Cu(II) and Fe(III) ions were determined by FAAS.

2.4. Sample preparation

Sampling should be made very carefully due to the low concentrations of analyte species in the environmental and biological samples. In this investigation, four water samples including well water, springwater, lake water, and tap water were used for determination of Fe(III) and Cu(II). The water samples were filtered through a 0.45-µm PTFE Millipore filter and kept in refrigerator until analysis.

3. Results and discussion

The base of the work is using modified nanopowder SnO_2 to retention of target metals in a surfactant-rich phase. In this work, dual cloud point extraction (dCPE) procedure was used together with SPE instead of regular CPE to enhance the accuracy.

3.1. Effect of pH on the proposed procedure

The pH is evaluated as a critical parameter for regulating the partitioning of the analyte in the surfactant-rich phase which seems to control the extraction efficiency [32]. Additionally, in SPE studies, pH has also an important impact on the surface charge of adsorbents. The effect of pH on the extraction of Fe (III) and Cu(II) ions was studied using a series solution in the range of 1.0–9.0. As can be seen in Fig. 1, quantitative recoveries (>95%) were obtained for both studied ions beyond $pH > 6.0$. So, the pH 6 was selected for next experiments. There is a considerable reduction in the recoveries at lower pHs than 5.5 as a result of the positive charge of the SnO_2 surface in the acidic media which repulse the positive charges of analytes. On other hand, in low pH values, the extraction efficiency is very low because the complex formation rate is very slow [33]. In addition, pH is one of the characteristics which affects the adsorption capacity of media. Also, the pH affects redox potential of adsorbate and surface charge or better known as the point of zero charge (pH_{pzc}) of the adsorbent. The surface of the adsorbent will have a positive charge at pH lower than pH_{pzc} and will attract negatively charged ions (anions) present in the solution. As the pH of the system increases, the number of positively charged sites decreases and the number of negatively charged sites increases, leading to a attraction between cationic metals and anionic surface. The pH_{pzc} value for SnO_2 nanopowder is 5.5 [34]. As the alkalinity increases, the ionizable surface groups are inclined to lose their protons resulting in the surface with negative charge. This fact causes to increase the amount of caught metal species owing to the enhancement of electrostatic attraction.

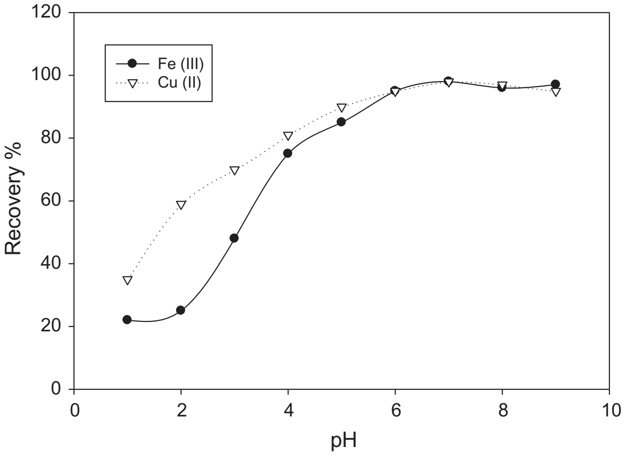

Fig. 1. The effect of pH on the recoveries of the metal ions.

3.2. Effect of amount of chelating agent

Selective and suitable chelating agents are very important for analytical determination and preconcentration experiments. We selected Amaranth dye as chelating agent in order to obtain efficient extraction recovery due to good chelating capacity. Various quantities of Amaranth (5–30 mg) were investigated for an appropriate modification of the SnO_2 adsorbent. As presented in Fig. 2, the recoveries of analyte ions increased with increasing amounts of amaranth up to 20 mg and reached a constant 95% value of recovery. Extraction efficiency was remained firm beyond 20 mg and not observed a meaningful change. Hence, 20 mg of Amaranth was selected for subsequent studies. At lower concentrations, the amount of ligand is probably insufficient to extract all ions in the solution. The majority of metals have a positive charge in the studied pH range. Therefore, the adsorption of metal ions on nanopowder is increased due to the progressive ionization of the surface functional groups. This implies an increase in the density of the surface negative charge due to the ionization of anionic dye sulfonate groups, producing greater adsorption for Cu(II) and Fe(III) [35]. That is, the adsorption of metal ions is increased due to the progressive ionization of the surface.

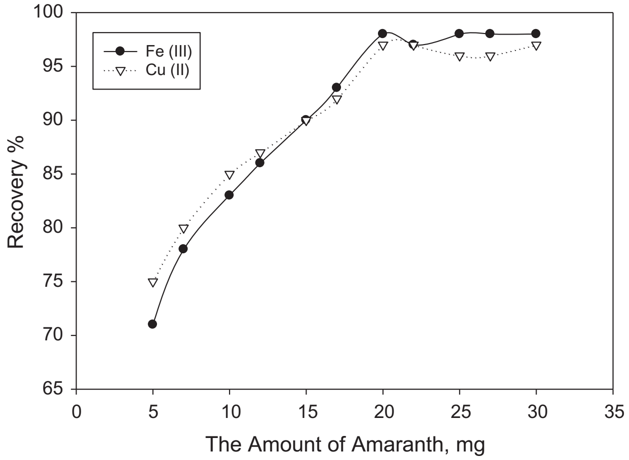

Fig. 2. The effect of Amaranth on proposed method.

3.3. Effect of amounts of adsorbent (SnO_2 nanopowder)

The amount of adsorbent is another critical factor in order to acquire quantitative recovery. Hence, the amount of modified SnO_2 nanopowder on the recoveries of Cu(II) and Fe(III) ions was optimized in the range of 1–20 mg. As can be seen in Fig. 3, recoveries of metal ions increased with increasing amounts of adsorbent up to 7 mg, and after that, it nearly remained constant. Thus, 7 mg of the adsorbent was applied in further experiments.

3.4. Effect of eluent type and volume

The type and concentration of eluent were also important factors on desorption of the analytes from the nanopowder. Since the lower volume of eluent has positive impact on preconcentration value, therefore, a suitable eluent should effectively elute the analytes from the nanopowder with possible the smallest volume. The effects of different eluents (nitric acid, hydrochloric acid, and acetic acid) were also investigated on the recoveries of Fe(III) and Cu(II) ions in order to the strip of target metal ions from modified SnO_2. The results revealed that nitric acid is the most appropriate eluent for this aim. In addition, various concentrations and volumes of the above-mentioned eluents were also examined for desorption of retained metal ions from the nanosorbent. The obtained results showed that HNO_3 was the best eluent because of better reproducibility and highest recovery of determinations. According to the experiments carried out by nitric acid at different concentrations, the recovery of the analytes enhanced with nitric acid concentrations until 2.0 mol L^{-1} and then remained nearly constant at the higher concentrations. The results indicated that 2.0 mol L^{-1} HNO_3 was sufficient for quantitative elution (>95%). The results were shown in Table 1. Furthermore, the influence of eluent volume (100–300 μL) on the recoveries was studied using 2.0 mol L^{-1} HNO_3. By adding 200 μL of 2.0 mol L^{-1} HNO_3, quantitative recoveries were obtained for all analyte ions. The recoveries were not quantitative for the other eluents listed in Table 1. Therefore, 200 μL of 2.0 mol L^{-1} HNO_3 was used as eluent for further work.

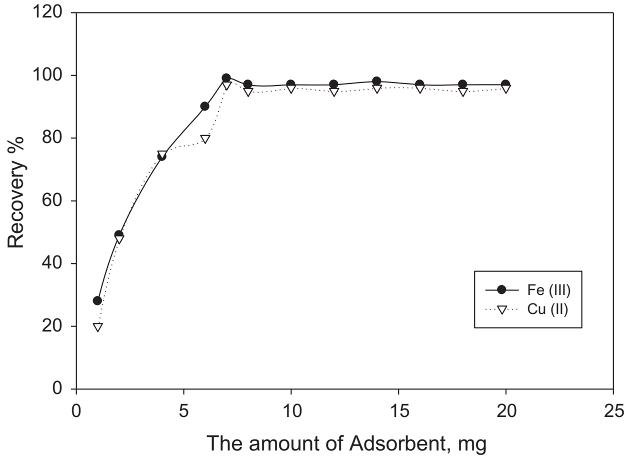

Fig. 3. Effect of amount of adsorbent on the recoveries of analytes.

3.5. Effect of the sample volume

Since concentrations of metal ions are very low in real samples, these analytes should be brought to levels which can be determined by instrumental

Table 1
The effect of various eluents on the analyte ion recoveries (optimum conditions: pH: 6; eluent: 0.2 mL; sample volume: 30 mL)

Eluent	Recovery (%) Fe(III)	Cu(II)
1 mol L^{-1} HCl	89 ± 0.8	91 ± 1.1
2 mol L^{-1} HCl	91 ± 3.1	90 ± 2.9
3 mol L^{-1} HCl	92 ± 2.5	89 ± 1.8
1 mol L^{-1} HNO_3	91 ± 2.8	90 ± 1.2
2 mol L^{-1} HNO_3	99 ± 1.9	98 ± 1.4
3 mol L^{-1} HNO_3	92 ± 3.1	93 ± 2.6
1 mol L^{-1} CH_3COOH	73 ± 2.0	70 ± 3.2
2 mol L^{-1} CH_3COOH	75 ± 1.0	78 ± 2.3
3 mol L^{-1} CH_3COOH	79 ± 1.7	75 ± 3.2

techniques. For this purpose, one of the most used ways is the extraction of target species into smaller volumes from larger volume. Therefore, the maximum volume of sample solution was investigated by increasing the volume of metal ion solution in the range of 5–50 mL. The effects of sample volumes on the recoveries of the two analytes were shown in Fig. 4. The results showed that the maximum sample volume could be up to 30 mL with the recovery >95%. Therefore, 30 mL of sample solution was adopted for the preconcentration of analytes from sample solutions. The preconcentration factor (PF) can be calculated using volume ratios (30 mL/0.2 mL) as 150.

3.6. Effects of type and concentration of non-ionic surfactant

In this study, the surfactant works as a dispersing agent in relation with modified SnO_2 nanopowder as well as entrapping agent for CPE. Triton X-114 and Ponpe 7.5 were investigated in order to examine the influence of non-ionic surfactants on efficiency of method. The effects of these surfactants were examined using a series solutions in the range of 0.5–1.5%. As can be seen in Fig. 5, the high recovery values were obtained with Triton X-114. In addition, the maximum recovery was obtained at the concentration of 1.0%. Hence, Triton X-114 was chosen and used for next studies.

3.7. Effect of equilibrium temperature and time

It is essential to optimize the equilibration temperature and incubation time in order to obtain simple phase separation and efficient preconcentration. It is favorable to use the shortest incubation time and the lowest possible equilibration temperature. Heating is necessary to separate the phases and causes an efficient extraction in CPE. Moreover, non-ionic surfactants appear relatively more hydrophobic at higher temperatures, due to an equilibrium shift that favors dehydration of the ether oxygen. This leads to an increase in the number concentration of micelles. Therefore, the solubilization capability of the micellar solution increases with temperature leading to an increase in the extraction. Additionally, volume of coacervate phase decreases with temperature [36]. So, the impact of the equilibration temperature was investigated by various temperatures from 20 to 70°C. The outcome revealed that the maximum efficiency was attained for 45°C. According to experimental observations, the extraction efficiency was decreased at higher temperatures than 45°C. The possible reason for this decrease can be explained with instability of complexes. Therefore, 45°C was chosen as equilibration temperature. The dependence of extraction efficiency upon incubation time was also studied over the time period of 2–20 min. An incubation time of 5 min was adequate for the highest absorbance.

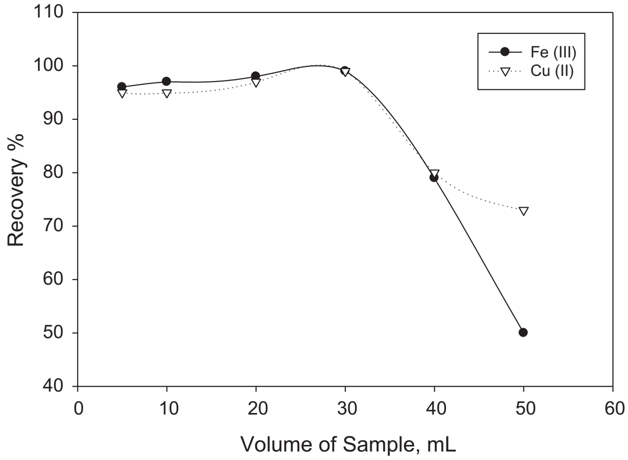

Fig. 4. Effect of sample volume on the recoveries of analytes.

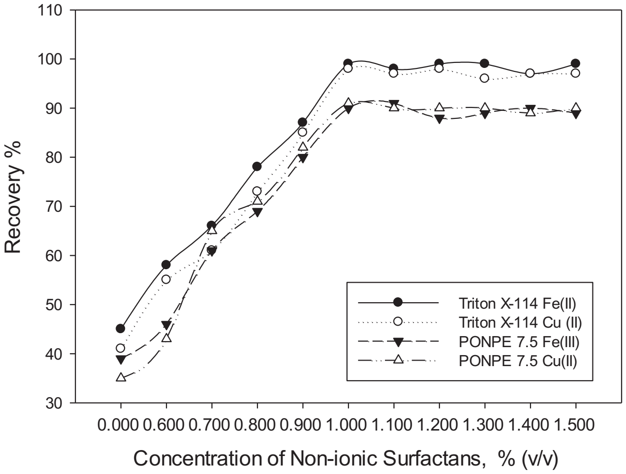

Fig. 5. The effect of non-ionic surfactants on the proposed method.

3.8. Effect of salt

It has been reported that the addition of electrolytes may accelerate the separation of the two phases of the CPE procedure. Cloud point temperature can be decreased by ionic salts due to salting-out effect. Because the salts promotes the dehydration of the ethoxy groups of Triton X-114 on the outer surface of the micelles [36]. Additionally, the salting-out effect helps to reduce the equilibrium temperature needed for phase separation. Several ionic salts such as Na_2SO_4, NaCl, and KCl were used in order to see their effects on CPE efficiency. The change of extraction efficiency related with salt concentrations can be seen in Fig. 6. So, the results showed that the best extraction efficiency was obtained in the presence of Na_2SO_4 for both ions. The salting-out ability of the cations and anions follows the Hofmeister series ($Na^+ > K^+$), ($SO_4^{2-} > Cl^-$) and can be related to the ions from Gibbs' free energy of hydration. SO_4^{2-} shows salting-out effect as it attracts and structures the water molecules and strengthens the hydrophobic interaction better than Cl^-. Additionally, the formal charge density on the anion SO_4^{2-} is more than Cl^- [37]. The fractional coacervate phase volume also decreases with salt concentration. Due to salting-out effect, more water goes to the dilute phase, decreasing the volume of the coacervate phase. Additionally, the salting-out effect is more pronounced for divalent salts as compared to monovalent ones [36].

The effect of electrolyte concentration on the extraction of the metals was examined by various amounts of salts in the range of 0.005–0.040 mol L^{-1}. The results showed that the maximum salt could be up to 0.015 mol L^{-1} with the recovery >95%, and after that, recoveries were not under quantitative amount. This opposite behavior of the salts could be due to increasing Na^+ in the solution and acting as a competitor for the target metals in getting attracted on the modified adsorbent.

3.9. Effect of foreign ions

In order to demonstrate the applicability of the method, the effect of common matrix ions which may interfere with the determination of Fe(III) and Cu(II) was examined. The obtained results were presented in Table 2. The tolerance limit is defined as ions had no significant interferences in the preconcentration and determination of the analyses. These results demonstrate that the method has a good tolerance to interference and is suitable for Fe(III) and Cu(II) detection in the real samples.

3.10. Adsorption capacity

The adsorption capacity of the newly developed adsorbent was also examined and calculated in the order to present an idea for removal studies. For this purpose, 0.1 g of adsorbent was added to 50 mL of solution comprising 1.0 mg of metal ion in the presence of pH 6.0 buffer and shaken for 30 min, and after that, the mixture was filtered. Then, the supernatant solution was diluted to 100 mL and determined by flame atomic absorption spectrometry. This procedure was repeated for each analyte ions separately. The capacity of modified SnO_2 nanopowder for Fe(III) and Cu(II) was found to be 73.3 and 60.8 mg g^{-1}, respectively.

3.11. Analytical performance

Using the optimized experimental conditions, calibration curves were linear in the range of 0.23–100.00 μg L^{-1} for Fe(III) and 0.30–110.00 μg L^{-1}

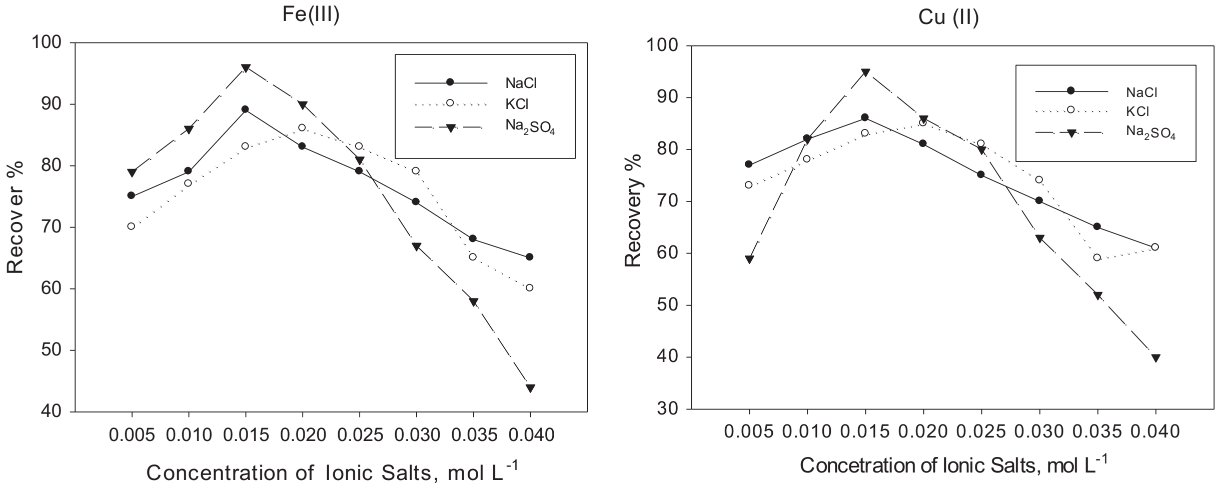

Fig. 6. The effect of ionic salt on extraction efficiency.

Table 2
Effect of interfering ions on the recoveries of Fe(III) and Cu(II) ions (40 μg L^{-1})

Ions	Concentration (mg L^{-1})	Recovery (%)[a] Fe(III)	Recovery (%)[a] Cu(II)
Ag^+, K^+, Na^+, Cl^-, Li^+, I^-	10,000	97 ± 2	98 ± 2
Mg^{2+}, Ca^{2+}, CO_3^{2-}, $C_2O_4^{2-}$	8,000	96 ± 1	97 ± 1
SO_4^{2-}, F^-	6,000	96 ± 3	97 ± 3
HCO_3^-,NO_3^-	3,000	99 ± 1	99 ± 1
PO_4^{3-}, H_3CCOO^-	1,500	97 ± 3	96 ± 2
Sn^{4+}, Ni^{2+}, Pb^{2+}	500	96 ± 2	97 ± 2
Mn^{2+}, Cd^{2+}, Mo^{5+}	250	97 ± 1	97 ± 1
Hg^{2+}, Pd^{2+}, Zn^{2+}	100	99 ± 2	99 ± 3
Sn^{2+}, Al^{3+}, Cr^{3+}	10	98 ± 3	99 ± 1

[a]Mean ± standard deviations.

Table 3
The results for determination of Fe(III) and Cu(II) in various water and CRM samples ($N = 5$)

Samples	Added (μg L^{-1})		Found[a] (μg L^{-1})		Recovery (%)		RSD (%)	
	Fe(III)	Cu(II)	Fe(III)	Cu(II)	Fe(III)	Cu(II)	Fe(III)	Cu(II)
Well Water	–	–	28.21 ± 0.05	25.14 ± 0.08	–	–	2.5	2.6
	50	50	78.17 ± 0.02	73.74 ± 0.09	99.96	98.14	1.3	1.1
	100	100	127.87 ± 0.07	127.81 ± 0.08	99.73	102.13	2.5	1.8
SpringWater	–	–	25.10 ± 0.03	29.12 ± 0.02	–	–	1.5	2.6
	50	50	74.84 ± 0.09	81.25 ± 0.08	99.65	102.65	3.0	1.8
	100	100	125.29 ± 0.06	128.30 ± 0.07	100.15	99.36	3.0	1.8
Lake Water	–	–	24.47 ± 0.01	20.58 ± 0.02	–	–	2.0	3.5
	50	50	75.93 ± 0.05	68.78 ± 0.02	102.02	97.45	1.4	2.3
	100	100	124.12 ± 0.03	120.12 ± 0.01	99.71	99.62	2.8	1.4
Tap Water	–	–	8.49 ± 0.06	6.21 ± 0.03	–	–	1.1	3.1
	10	10	17.91 ± 0.02	16.76 ± 0.07	96.86	103.39	1.4	2.1
	20	20	27.19 ± 0.09	26.40 ± 0.08	103.74	100.72	1.8	2.0
SRM[b] analysis	Certified value (μg L^{-1})		Found[a] (μg L^{-1})		RE (%)		RSD (%)	
	Fe(III)	Cu(II)	Fe(III)	Cu(II)	Fe(III)	Cu(II)	Fe(III)	Cu(II)
TM-25.3	29.5	27.6	28.45 ± 0.09	26.88 ± 0.12	3,6	2,6	2.1	1.1
TM-28.3	16.5	6.15	15.91 ± 0.01	6.34 ± 0.07	3,6	−3,1	2.5	3.4
TMDA 61	81.1	69.2	84.1 ± 0.02	67.30 ± 0.03	−3,7	2,7	1.0	1.1
TM-DWS.2	223	167	222.23 ± 0.09	166.66 ± 0.06	0,3	0,2	2.4	3.1

[a]$\bar{x} \pm ts\sqrt{n}$ at 95% confidence ($N = 5$).
[b]Environment Canada CRMs.

for Cu(II). The detection limits, based on three times of the standard deviation of 10 runs of blank solution, were found to be 0.07 and 0.09 μg L^{-1} for Fe(III) and Cu(II), respectively. The relative standard deviation (RSD), resulted from nine determinations of 1.0 μg L^{-1} of Fe(III) and Cu(II) were 2.1 and 3.9%, respectively. The linear regression equations were Abs = 0.01527 [Fe(III)]+ 0.00492 and Abs = 0.01477 [(Cu)] + 0.00338. The correlation coefficients for Fe(III) and Cu(II) were 0.9998 and 0.9996, respectively. The PF for the proposed method was 150 using phase ratios.

Table 4
Comparison of the proposed method with recent studies reported in literature using nanoparticles as adsorbent

Analytes	System	Medium	Eluent	PF[a]	LOD[b] (μg L $^{-1}$)	References
Cd^{2+}, Cu^{2+}, Cr^{3+} Mn^{2+}	Fe3O4@SiO2@TiO_2/magnetic nanoparticle	pH 8.0	0.5 M HNO_3	–	1.6–4.0	[14]
Cu^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Cd^{2+}, Cr^3	TiO_2 nanoparticles/column	pH 8.5	2. 0 M HCl	–	0.06–0.36	[16]
Cd^{2+}	B_2O_3/TiO_2 nanoparticles	pH 6.0	1.0 M HCl	50	1.44	[18]
Ni^{2+}	TiO_2 nanoparticles/Tan/1-hexadecyl-3-methylimidazolium bromide	pH 10.0	1.0 (HNO_3)	50	0.80	[21]
Cr^{6+}	Multiwalled carbon nanoparticles/speciation/ammonium pyrrolidine dithiocarbamate (APDC) and oxidation of Cr^{3+}/column	pH 2.0	1.0 (HNO_3)	100	0.9	[38]
Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}	TiO_2 nanoparticles with different dimensions/cartridges	pH 7.5	Acetonitrile	20	5–20	[39]
Cd^{2+}, Ni^{2+}	TiO_2 nanoparticles/8-hydroxyquinoline/column/	pH 9.0	0.5 M HNO_3	50	0.25–1.0	[40]
Cu^{2+}, Fe^{3+}	SnO_2 nanopowder/modified by amaranth/cloud point	pH 6.0	2 M HNO_3	150	0.07–0.09	This work

[a] PF: Preconcentration factor.

[b] LOD: Limit of detection.

3.12. Analytical applications

The method was applied for determination of Fe(III) and Cu(II) amounts in tap water, well water, springwater and lake water. Different quantities of analytes were also spiked to these water samples. The results showed that a good agreement was obtained between the added and measured Fe(III) and Cu(II) amounts (Table 3). The accuracy of the method was verified by the analysis of spiked samples and CRM analyses. These results indicated the suitability of Amaranth-SnO_2 nanopowder for sensitive preconcentration and determination of trace Fe(III) and Cu(II) in environmental samples.

4. Conclusion

In this work, modified SnO_2 nanopowder was applied for simultaneously preconcentration and determination of Fe(III) and Cu(II) ions using dCPE and SPE approaches together. This article proved that the usage of modified SnO_2 nanopowder and surfactants had excellent ability for determination of Cu(II) and Fe(III) in environmental water samples. High sensitivity, selectivity, lower detection limits, and high PF are important properties which is comparable or higher than the other extraction methods in literature are from the advantages of the proposed method [14,16,18,21,38,39,40]. Table 4 shows a comparison among the proposed method and other previously reported methods.

The high accuracy of the proposed method was confirmed by recovery test and CRM analyses. The simplicity in operation, good precision, being economical, low extraction time and the lake of the toxic solvents presence in the method are from other benefits of the work.

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