

Fe-Ni@ACC Nanocomposite for Magnetic Dispersive Micro Solid-phase Extraction of Cu (II) From Food and Hair Samples

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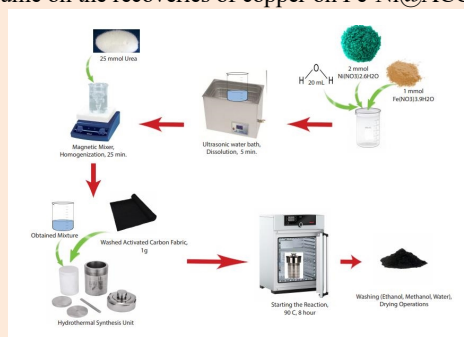
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ABSTRACT: Fe-Ni@ACC nanocomposite was synthesized by hydrothermal method and characterized using scanning electron microscope (SEM) and Fourier-transform infrared spectroscopy (FT-IR). Fe-Ni@ACC was used as adsorbent for magnetic dispersive micro solid-phase extraction (M-D- μ SPE) procedure for separation and preconcentration of trace level of copper at trace levels before its determination by microsampling flame atomic absorption spectrometry (FAAS). The effects of various parameters such as pH, amount of adsorbent, eluent type and eluent volume, and sample volume on the recoveries of copper on Fe-Ni@ACC were optimized. The presented method is accurate, inexpensive and environmentally friendly and due to magnetic properties of the adsorbent, the separation process is very simple and fast. The method presents limit of detection (LOD)(3s/m) of $0.69 \mu\text{g L}^{-1}$, limit of quantification (LOQ)(10s/m) of $2.29 \mu\text{g L}^{-1}$, preconcentration factor of 40 and relative standard deviation (RSD %) (s/x) 1.18%. The accuracy of the method was confirmed by the analysis of TMDA-53.3 fortified water and TMDA-64.2 fortified water certified reference materials and addition-recovery tests to real samples. The present M-D- μ SPE method was successfully applied to determination of copper level of tap water, cigarette, human hairs and black teas samples.



INTRODUCTION

Trace levels of heavy metals, which have significant positive and negative effects on the ecosystem and human health, are released into the environment through natural activities and/or human activities.¹⁻³ Copper at trace levels is of vital importance due to its duties in the biological systems of living things, on the other hand, high doses cause serious problems due to its toxicity. In the deficiency of copper which plays an important role in living metabolism, causes problems such as anemia, decrease in body resistance, weakness, fatigue, decreased growth, iron deficiency, fragile bones, skin scars, eczema, mitochondrial destruction, DNA breakage, injury to neuronal cells and deterioration in different -enzymes.⁴⁻⁷ The high amounts of copper can cause liver metabolic disorders, nausea, vomiting, diarrhea, stomach cramps, hepatic

neurosis, gastrointestinal bleeding, hypertension, dermatitis, Alzheimer's, Parkinson's, schizophrenia, depression, autism, epilepsy, liver or kidney damage, and even death occurs.⁸⁻¹² Copper enters the environment as a result of natural events such as volcanoes, forest fires and aerosol particles from sea spray. Its amount in the environment increases as a result of human activities in industrial areas such as electricity-electronics, paper, petroleum, rayon, water treatment, wood and leather preservative, mining, fertilizer, construction, transportation, industrial equipment, chemistry, jewelry and paint industry.^{2,13,14} Due to the fundamental significance and hazardous effects of copper on the ecosystem and living things, accumulating on biological, nutritional and environmental samples by being released into the environment; It is of great importance to determine copper at trace levels with accurate, sensitive, precise, economical, environmentally friendly and fast analytical instrumental methods.

Many analytical techniques such as FAAS, GF-AAS, ICP-OES, ICP-MS, SEC-ICP-MS, AES, voltammetry and spectrophotometry/derivative spectrophotometry have been developed for the determination of copper and the other metals amount in various samples.¹⁵⁻²² Flame atomic absorption spectrometry (FAAS) is a sturdy technique that gives accurate, sensitive and precise measurements found in many laboratories due to its low cost and ease of use.^{23,24} However, generally separation and enrichment are required prior to flame atomic absorption measurements due to low concentrations of trace level analytes and/or complex sample matrix. Thus, the analyte of interest is determined more precisely and with lower detection limit values.²⁵⁻²⁷ Many sample preparation methods such as solid phase extraction (SPE), liquid-liquid extraction (LLE), and cloud point extraction (CPE) have been developed for separation and enrichment of copper from complex matrix media.²⁸⁻³¹ However, all these classical methods have initiated to leave their position to microextraction methods because of the disadvantages such as time consuming, laborious, expensive, toxic, insufficient preconcentration factor, high organic solvent volume and secondary waste.³²⁻³³ For these disadvantages to eliminate, microextraction techniques developed such as liquid phase micro extraction (LPME) and magnetic dispersive micro solid-phase extraction (M-D- μ SPE), which offer the advantages of environmentally friendly, simple, fast, cheap, high preconcentration factor, high analyte recovery, minimal analyte loss and low volume toxic solvent use.^{2,34-36}

The usage of new adsorbent on SPME of trace metal ions is one of the attractive parts of analytical chemistry. The Activated carbon cloth (ACC) is one of them. It has some advantages: mechanical robustness and resistance, higher surface area, easy handling, modification and regeneration compared to the other activated carbon products.³⁷⁻⁴⁴ All these features make ACC an economical and highly efficient an adsorbent that can be used in solid phase extraction and dispersive micro solid-phase extraction methods. The synthesis and characterization of new nanocomposites containing ACC is one of the new working areas of our working group to improve adsorption properties of ACC. Fe-Ni@ACC nanocomposite is one of them, it was firstly synthesized and used for SPME of copper (II). The adsorption mechanism related with physical interaction between Fe-Ni@ACC nanocomposite and analyte ion.

In this study, Fe-Ni@ACC nanocomposite was synthesized and characterized and used as an adsorbent in the separation and enrichment of Cu (II) in various samples by SPME method. The analytical parameters (pH, adsorbent amount, eluent volume, sample volume, foreign ion effect, *etc.*) affecting the quantitative recoveries of copper were optimized.

Fig. 1 a,c,e- ACC SEM images, b,d, f- Fe-Ni@ACC SEM images.

Fig. 2 SEM-Energy dispersive X-ray (SEM-EDX) spectrum of the Fe-Ni@ACC nanocomposite.

Fig. 3 SEM Mapping images of the Fe-Ni@ACC.

EXPERIMENTAL

Characterization of Fe-Ni@ACC Nanocomposite. A nanocomposite of activated carbon cloth with Ni-Fe was prepared by a one-step hydrothermal method and this nanocomposite was used as a sorbent in the microextraction of trace levels of Cu (II). The activated carbon cloth and the obtained nanocomposite were characterized using SEM (Fig. 1), EDX (Fig. 2), SEM mapping (Fig. 3) and FT-IR (Fig. 4). When the SEM images with the same

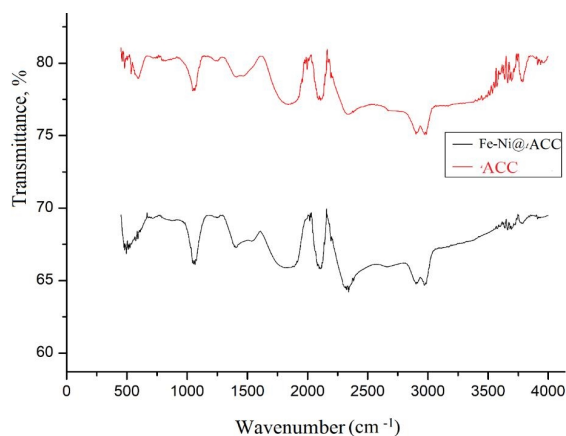


Fig. 4 FT-IR spectrum of ACC and Fe-Ni@ACC nanocomposite.

Table 1. SEM-EDX results of Fe-Ni@ACC nanocomposite

Elements	Weight (%)	Atomic (%)
C	78.34	84.31
O	18.55	14.99
Fe	1.36	0.32
Ni	1.74	0.38

magnification ratio in Fig. 1 are examined comparatively, it can be easily seen that Ni-Fe grows the ACC surface by densely covering. In addition, it is seen that the nanolayers preserve the nanofiber morphology and the surface enlarged with Ni-Fe becomes more specific and active. Therefore, it is more accessible to analyte ions when used as a sorbent. The physical interaction between surface of the nanocomposite and analyte ions are effective. For the characterization of Fe-Ni@ACC nanocomposite, EDX analysis was performed and elemental composition data of the nanocomposite were obtained. The presence of Fe and Ni elements in the obtained Fe-Ni@ACC nanocomposite was verified and the results are presented in Figure 1. Peaks belonging to Fe and Ni elements are observed and these peaks prove their existence in the nanocomposite. In addition, both weight and atomic weight-based amounts of elements in nanocomposite structure were determined in % aspect by SEM-EDX analysis and the results are presented in Table 1. Both the table data and the data in the figure show that while a large part of the element composition belongs to the element carbon (C) from the activated carbon cloth, a small part belong to the elements Fe and Ni. According to SEM elemental mapping (Fig. 3) results on the Fe-Ni@ACC Nanocomposite shows the existence of elements Fe, Ni and C, and homogeneous distribution of Ni and Fe at micrograph. Although the metals shed in small parts in the coating and the metal density decreases, it is generally seen in the SEM mapping that the ACC is covered with Fe and Ni. SEM mapping images support SEM EDX results.

The FT-IR spectrum of the 4000-500 cm^{-1} infrared spectral region of Fe-Ni@ACC is presented in Fig. 4. The peaks at ~ 2978

cm^{-1} and $\sim 2896 \text{ cm}^{-1}$ are due to the C-H stretchings in the (-CH₂) and (-CH₃) groups. The peak at $\sim 2100 \text{ cm}^{-1}$ corresponds to the C=C bond stretching, and the peak at $\sim 1043 \text{ cm}^{-1}$ corresponds to the C-O stretching vibration.⁴¹ In the FT-IR spectrum at finger print region, while the peak of the FeO bond is seen between 500-750 cm^{-1} , the peak of the NiO bond is seen between 500-550 cm^{-1} .⁴⁷⁻⁴⁸ Stretching peaks between 500-750 cm^{-1} in Fe-Ni@ACC are due to FeO and NiO.⁴⁹⁻⁵¹

Effect of pH. pH of the working solution is one of the most important variables controlling which the adsorption of metals to sorbent materials, hence the percentage recovery and SPME efficiency.^{38,52} The effect of pH on the SPME method was studied in the range of 2.0-11.0 using a model solution in which other parameters were kept constant. The results are presented in Fig. 5a. The quantitative recovery values between pH 8.0-10.0 were obtained. The recoveries were not quantitative in the neutral and acidic pH. All subsequent work was done at pH 9.0 using phosphate buffer solution.

Effect of Fe-Ni@ACC Amount. The amount of sorbent in SPME methods is another important parameter that effects the quantitative recovery values of the analyte elements.⁵³ The effects of Fe-Ni@ACC amounts on the recoveries of copper(II) were investigated in the range of 1.0-20.0 mg. The results are depicted in Fig. 5b. It is seen that the quantitative recovery values were obtained as from 5.0 mg sorbent. In further works, 5.0 mg of Fe-Ni@ACC was used. The Fe-Ni@ACC adsorbent was stable to acids and bases and it was used at least 20 times without any loss of its adsorption properties.

Effect of Eluent Type and Concentration on recoveries of copper(II). The most suitable eluent to desorb metal ions on the surface of the adsorbent should be determined.⁵⁴ The desorption occurs when the desorption power of the eluent is higher than the adsorption force that keeps Cu (II) ions on the sorbent.⁴⁰ In the presented study, 1, 1.5, 2, 3 M HNO₃ and 1, 1.5, 2 M HCl were tested as eluent. The results are given in Fig. 5c. It was observed that a quantitative % recovery was obtained with 2 M and 3M HNO₃. So, 2 M HNO₃ was selected in further studies.

Effect of Eluent Volume. The effect of eluent volume on the recoveries of copper(II) was studied using 2 M HNO₃ in the range of 0.5-2.0 mL. The results are presented in Fig. 5d. The maximum and quantitative recovery of Cu (II) ion is at volumes of 0.75 mL and higher. Therefore, the optimum eluent volume was determined as 0.75 mL.

Effect of sample volume. The determining the maximum sample volumes is an important goal to achieve high preconcentration factor in the extraction processes of trace element analysis.⁵⁵ The effect of sample volume on the method was investigated using model solutions in the range of 10.0-50.0 mL. The results given in

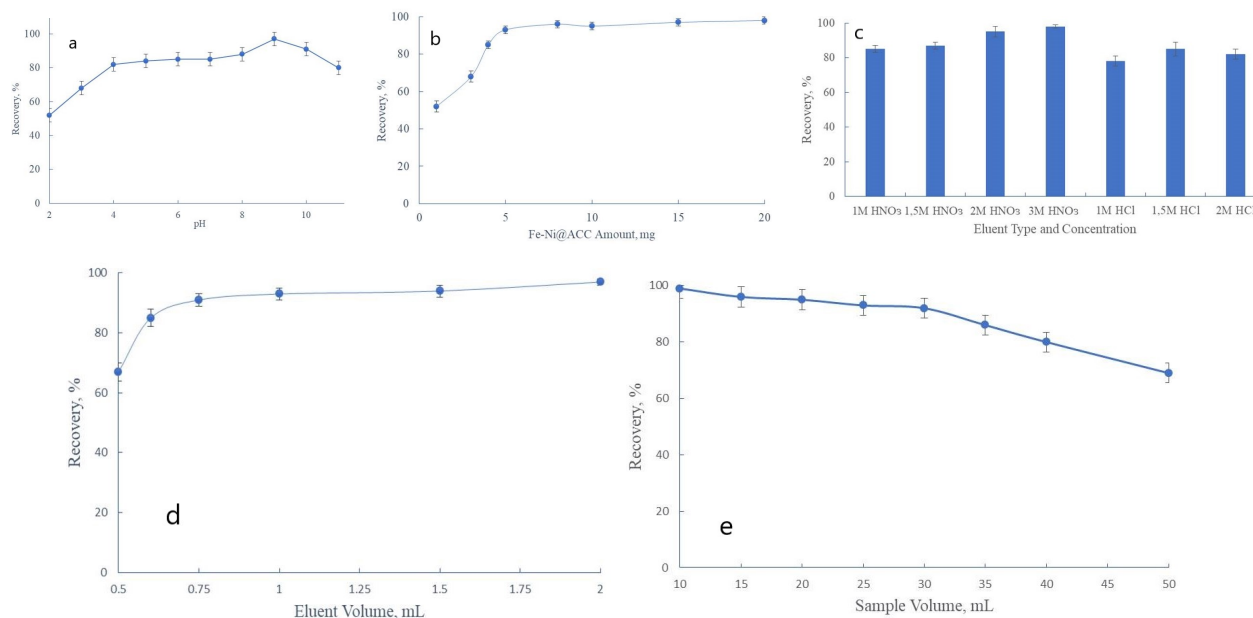


Fig. 5 (a) Effect of pH on the recovery, % of copper (N = 3); (b) Effect of Fe-Ni@ACC amount on recovery efficiency of Cu (II) ions (pH: 9, N=3); (c) Effect of eluent type and concentration on recovery efficiency of Cu (II) ions (pH: 9, Fe-Ni@ACC amount: 5 mg, N=3); (d) The effect of eluent volume on the % recovery efficiency of Cu (II) ions (pH: 9, Fe-Ni@ACC amount: 5 mg, eluent: 2M HNO₃, N=3); (e) The effect of sample volume on % recovery efficiency of Cu (II) ions (pH: 9, Fe-Ni@ACC amount: 5 mg, eluent type: 2M HNO₃, eluent volume: 0.75 mL, N=3).

Table 2. The effect of some foreign ions on the % recovery efficiency of Cu (II) ions (pH: 9, Fe-Ni@ACC amount: 5 mg, eluent type: 2M HNO₃, eluent volume: 0.75 mL, N=3)

Foreign Ions	Added as	Conc. ($\mu\text{g mL}^{-1}$)	Recovery (%)
Ca ²⁺	CaCl ₂	250	93 ± 2
F ⁻	NaF	500	94 ± 2
Na ⁺	NaNO ₃	250	92 ± 1
Mn ²⁺	Mn(NO ₃) ₂ · 4H ₂ O	10	94 ± 2
Pb ²⁺	Pb(NO ₃) ₂	5	93 ± 1
Co ²⁺	Co(NO ₃) ₂ · 6H ₂ O	10	97 ± 1
K ⁺	KCl	1500	95 ± 1
Mg ²⁺	MgCl ₂ · 6H ₂ O	100	95 ± 1
Fe ³⁺	Fe(NO ₃) ₃ · 9H ₂ O	5	92 ± 1
SO ₄ ²⁻	Na ₂ SO ₄	2000	96 ± 2
CO ₃ ²⁻	Na ₂ CO ₃	2500	95 ± 3

Table 3. Analysis of water certified reference materials (CRMs) with the developed M-D- μ SPE method (pH: 9, Fe-Ni@ACC amount: 5 mg, eluent type: 2M HNO₃, eluent volume: 0.75 mL N=3)

Water CRMs	Certification value ($\mu\text{g L}^{-1}$)	Found value ($\mu\text{g L}^{-1}$)	Relative Error (%)
TMDA-53.3	308	312 ± 12	1.3
TMDA-64.2	274	273 ± 8	0.36

Fig. 5e shows that up to 30 mL of quantitative % recovery was achieved. The maximum sample volume was chosen as 30 mL and the preconcentration factor was calculated as 40 when the final volume was 0.75 mL.

Matrix effects. The levels of foreign ions accompanying analyte ions in real samples are a problem that significantly affects the % recovery of the analyte and the efficiency of the extraction

procedure.⁵⁶⁻⁵⁹ In Table 2, the effects of some foreign ions on the method at the given concentrations are examined. The obtained quantitative % recovery values show that examined the foreign ions do not affect the developed method at the specified concentrations.

Analytical performance of the method. Analytical data, which are indicators of analytical performance, were obtained under optimum experimental data, and 10 parallel blank samples were prepared and the developed method was applied to determine the limit of detection (LOD) and limit of quantification (LOQ). Recovery for copper up to sample volume of 30 mL is quantitative and since the final volume was 0.75 mL, the preconcentration factor was calculated as 40. The limit of detection (LOD) of the method was calculated as $0.69 \mu\text{g L}^{-1}$ at 3s/m, and the limit of quantification (LOQ) was calculated as $2.29 \mu\text{g L}^{-1}$ at 10s/m. The 40-fold enrichment factor was taken into account in the calculations. Relative standard deviation (%RSD) was calculated as 1.18% from the formula $100 \times (s/x)$ (N=10). The calibration curve obtained for the method, $y = 0.0772x + 0.0009$ (y=concentration, x=absorbance) and R^2 is 0.9997. The obtained % recovery values in real sample applications of the method are in the range of 94-103 (s: standard deviation of the blank signals (N=10), m: slope of the calibration curve).

To evaluate the accuracy of the developed SPME method, the method was applied to Environment Canada TMDA-64.2 Fortified water and Environment Canada TMDA-53.3 Fortified Water certified reference materials and the results are presented in Table 3. When the obtained results are compared with the Cu (II)

concentration in the certified reference material, it is seen that both are compatible.

Real samples analysis. Addition and recovery studies were carried out on tap water, cigarette, human hairs and black teas samples for to investigate the applicability of the developed SPME method. A known amount of analyte was added to these samples and the developed method was applied. The results are presented in [Table S1](#) and [Table S2](#). As can be seen from the tables, recoveries ranging from 94-103% were obtained, which is an acceptable range for trace analysis.

Comparison with other methods. This developed method was compared with other studies in the literature in which AAS/FAAS was used in terms of preconcentration factor, detection limit, relative standard deviation values and other data, and the data are presented in [Table S3](#). It has been seen that the data in the Table and the obtained data are comparable.^{2,6,38,60-65}

CONCLUSION

A new method magnetic dispersive micro solid-phase extraction has been developed which includes a combination of M-D- μ SPE and FAAS for the separation, preconcentration and determination of trace level Cu (II) founds in various black tea, cigarette, human hair and water samples. The analytical parameters effective on the method have been optimized and the results are presented above. In order to test the accuracy of the developed method, both addition-recovery studies and certified reference material analyzes were carried out. The main advantages of the method can be listed as follows: offers low LOD and LOQ. High reproducibility and microextraction efficiency, the accuracy of the method has been demonstrated by the application to certified reference materials. The used amount of adsorbent and the volume of eluent are at a minimum level, can be analyzed by micro-injection, Completion of all steps of the method in a short time and easily, it can be applied to samples with different matrix (Black tea, water, cigarette and hair). An effective enrichment can be made with milligram-level adsorbent and this adsorbent can be used at least 20 times, *etc.*

ASSOCIATED CONTENT

The supporting information ([Tables S1–S3](#)) is available at www.at-spectrosc.com/as/home.

AUTHOR INFORMATION



Prof. Mustafa Soylak is working on Environmental Analytical Chemistry, Nanotechnology, Nanomaterials, Nanocomposites, Separation/Preconcentration Techniques including Solid Phase Extraction, Coprecipitation, Cloud point extraction, membrane filtration, speciation and microextraction of trace organic and inorganic species. Dr. Soylak

has an h-index of 111 (Web of science). He has over 725 papers in Web of Science, 8 book chapters and reviews, two textbooks (in Turkish), one textbook on microextraction techniques (Elsevier, 2020). He is Editor-in-Chief of Comprehensive Sampling and Sample Preparation (Elsevier, 2022). He was visiting professor at King Saud University- Saudi Arabia on 2010-2016 and at Near East University-Cyprus on 2018-2019. He is now Professor at Erciyes University, Department of Chemistry, Kayseri-Turkey. He is the editorial board member of *Atomic Spectroscopy*, *Journal of Hazardous Materials*, *International Journal of Environmental Analytical Chemistry*, *Arabian Journal of Chemistry*, *Turkish Journal of Chemistry* and *Journal of Nanostructure in Chemistry*. He has TUBITAK (Turkish Scientific and Technological Research Council) Encouragement Award in 2001. He is the recipient of the highest prestigious science award in Turkey, TUBITAK Science Award in 2020. He has also İlim Yayma Award from İlim Yayma Foundation in 2021. He has been a principal member of the Turkish Academy of Sciences (TUBA) since 2020. He has obtained a TÜBİTAK 2247-A National Fellowship for Outstanding Researchers (2021).

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Notes

The authors declare no competing financial interest.

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