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Using *Ghezeljeh* Nanoclay for Measuring of Copper Ions Released from the Cooking Pot into Food Samples by FAAS and ICP-AES

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Abstract

Ghezeljeh montmorillonite nanoclay was used as a natural adsorbent to measure and remove copper ions released from the cooking pot into food by applying the solid phase extraction (SPE) method in batch mode. The clay is characterized by using fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and X-ray diffractometry (XRD). The results of XRD and FT-IR of nanoclay confirm that montmorillonite is the dominant mineral phase. Based on SEM images of clay, it can be seen that the distance between the plates is Nano. The adsorbent was prepared using the *Galehouse* method and then a number of effective parameters on extraction were optimized using standard solutions: amount of adsorbent, eluent characteristics, pH and type of the buffer solutions, shaking time, adsorption temperature, volume of the standard solutions, and initial metal ion concentration. Also, the role of desorption and centrifugation time were explored. The limit of detection and quantification, preconcentration factor, and the adsorption capacity of the nanoclay were calculated. The method was applied to a variety of food materials to verify its efficiency. Subsequently, this method was applied to two Iranian stews cooked in copper pots plated with tin in order to measure the amount of copper released from the pot. The result suggests that the amounts of released copper and tin exceeded the tolerable daily intakes. In general, the removal of metal ions using the nanoclay proved to be rapid, efficient, reliable, and reproducible.

Key words: *Ghezeljeh nanoclay, Montmorillonite, Copper, Solid phase extraction.*

Introduction

Copper is an important nutrient which can be found in meat, shellfish, nuts, dried legumes, and cocoa. This element is absorbed through the stomach and proximal duodenum and plays an essential role in physiological processes

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such as growth, development, and wound healing. Copper deficiency, though relatively uncommon in human beings, manifests itself as anemia, neutropenia, thrombocytopenia, polyneuropathy, and ataxia [1]. Copper can be moderately toxic in humans, producing nausea, vomiting, diarrhea, and malaise. High concentrations of copper may lead to gastrointestinal irritation and necrotic changes in the liver and kidney. In severe copper poisoning by oral ingestion, these symptoms are soon followed by deep coma, oliguria, hepatic necrosis, and even death. In ancient Iran, copper pots were used to cook food. This practice is still common in Iran, and many manufacturers advertise copper pots. However, such utensils are plated with tin or stainless steel to avoid toxicity.

If copper utensils are not properly plated, this element can enter the food. Furthermore, we should make sure the coating is not damaged when washing or drying the utensil. Because of the harmful effects of excessive intakes of copper (and other heavy metals ions), it is necessary to determine their trace in food. One of the instruments commonly used for this purpose is flame atomic absorption spectrometry (FAAS). This technique is inexpensive and simple, but it usually cannot directly determine the trace of heavy metals at concentrations close to or lower than its limit of detection (LOD): the μgL^{-1} range [2, 3]. To resolve this problem, preconcentration-separation procedures have been proposed. Solid-phase extraction (SPE) is an attractive enrichment-separation process for heavy metal ions. It is trouble-free, high preconcentration factor, time- and price-saving, and can be directly used in microliter volumes without any sample loss [3, 4].

In the recent years, clay minerals as adsorbent for SPE have drawn much attention due to their distinctive features, such as ion exchange properties, its large specific surface area, high sorption capacity, swelling, intercalation behavior and their lower cost compared to synthesized materials (e.g. silica gel, zeolite) [5]. Dias et al. [6] used 2-mercaptobenzothiazole loaded on clays for SPE of Hg (II), Pb (II), Zn (II), Cd (II), Cu (II), and Mn (II) from an aqueous solution. Akcay and Kurtulmus [7] investigated adsorption position for uranium on Turgutlu and Kula clays. Krikorian and Martin [8] used modified clays for the SPE of copper (II), cadmium (II), silver (I), nickel (II), and lead (II) ions. Mohamed et al. [9] used Aswan clay from Egypt for speciation and preconcentration of Cr (III) and Cr (VI) from synthetic solution and tannery wastewater. Soylak et al. [2] used *Celtek* clay as adsorbent for separation-preconcentration of metal ions from environmental samples. Turan [10] investigated the uptake of trivalent chromium ions from aqueous solutions using kaolinite. Bhattacharyya and Gupta [4] investigated kinetic and thermodynamic removal of Cu

(II) by natural and acid-activated clays. Let us now give a brief review of the previous research into the issue of heavy metal ions in human food. Racz et al. [11] examined trace metals in culture mushrooms. Onianwa et al. [12] determined the concentrations of some trace metals in Nigerian dishes. Voegborlo et al. [13] investigated concentrations of Hg, Pb, and Cd in canned Tuna fish. Doner and Akman [14] determined the presence of iron and zinc in bulgur (boiled pounded) wheat by graphite FAAS. Ranau et al. [15] studied the presence of aluminum in fish smeared with aluminum folio. Fernandez et al. [16] reported trace element determinations of the Spanish tea. Tuzen [17] determined the concentrations of heavy metals in some fish samples.

This paper is a report on an investigation which attempted to measure and remove copper ions released from the cooking pot into food samples using *Ghezeljeh* montmorillonite nanoclay as the adsorbent. The nanoclay is readily obtainable, low-priced, environmentally friendly, and chemically and mechanically stable. It is interesting to note at this point that *Ghezeljeh* montmorillonite nanoclay (*Geleh-Sar-Shoor*) was used in ancient Persia to clean the body, notably the hair, and to bathe dead bodies prior to funerals ("Geleh-Sar-Shoor" means head-washing clay). This nanoclay is still used in some parts of Iran. The nanoclay was characterized using FT-IR, SEM, EDS, XRF and XRD. Based on SEM images of clay, it can be seen that the distance between the plates is Nano.

First, using standard solutions, a number of relevant parameters were optimized and copper ion recovery was determined. Then, the experimental method was applied to a variety of food materials to verify its efficiency and at a later stage to two Iranian stews cooked in copper pots plated with tin to measure the released copper.

Experimental

Reagents and solutions

All the reagents were purchased from the German company of Merck: acids, bases, hydrogen peroxide, sodium acetate, nitrate salts of copper, silver, lead, chromium, cobalt, cadmium, sulfate salts of aluminum, nickel, manganese, zinc, magnesium, chloride salts of sodium, potassium, iron, calcium, and ammonium. Since the reagents were of the highest purity, they were used without any further purification. The element standard solutions were produced by diluting a stock solution of 1000 mgL^{-1} of the specified element using doubly distillated water. Acetate buffer solution was prepared by combining appropriate volumes of 0.1 M acetic acid and 0.1 M sodium acetate at pH 4-6. Phosphate buffer solution was prepared using 0.1 M phosphoric acid at pH 7. Ammonium buffer solution was prepared by mixing suitable amounts of 0.1 M ammonia and 0.1 M ammonium chloride at pH 8-10. The pH of the buffer solutions was adjusted by adding 1 M NaOH or HCl, as needed. The *Ghezeljeh* montmorillonite nanoclay (adsorbent) was collected from *Ghezeljeh*, a village 18 km west of the city of *Tafresh* in Iran. This nanoclay, to the best of our knowledge, has not been used as adsorbent for the elimination of heavy metals from water, wastewater, and food. The food samples and also the ingredients of the two stews used in the experiments were all purchased from the local markets in *Qazvin* city, Iran.

Instrumentation

A model 420A digital Orion pH meter (Gemini, the Netherlands) equipped with a combined glass electrode was employed for pH adjustments. An ultrasonic water bath (Bandelin, Berlin, Germany) was used to disperse and disaggregate this clay. X-Ray Diffraction (XRD) data were obtained using an Ital Structures diffractometer (GNR, Novara, Italy), with Cu Kα radiation (40 kV/30 mA, λ= 1.542 A°). Fourier Transform Infrared (FT-IR) study was carried out using Tensor Bruker MIR-T27 (Germany) having a standard mid-IR DTGS detector. To quantitative measurements of copper ions a GBC 902 flame atomic absorption spectrometry (FAAS), (Dandenong, Victoria, Australia 3175) with deuterium background corrector and an air-acetylene flame was used. The working conditions in the FAAS spectrometer were adjusted according to the standard guidelines of the manufacturer.

To determine tin and aluminum concentrations, a Thermo Scientific ICP-AES (inductively coupled plasma atomic emission spectroscopy) (DUO 6500, England) spectrometer was used. Philips X-ray fluorescence (XRF) of the sample has been studied using XRF Analysis Instruments (Philips Magix Pro, Netherlands). A scanning electron microscope (SEM) (LEO 1450 VP, Thornwood, N.Y., USA) with variable pressure secondary electron detector and energy dispersive spectrometer operating (EDS) at 30 kV (Oxford INCA software, High Wycombe, U.K.) were used for SEM-EDX analysis.

Preparation of the adsorbent

The adsorbent was prepared using the *Galehouse* method [18]. Natural *Ghezeljeh* montmorillonite nanoclay was first treated with 0.1 M of acetic acid to eliminate carbonates, and then with 30% H_2O_2 to eliminate mineral and organic impurities. The nanoclay was carefully rinsed with doubly distilled water to eliminate traces of acetic acid and hydrogen peroxide. The treated nanoclay was dispersed and disaggregated in doubly distilled water through an ultrasonic water bath. The resulting suspension was transferred to a measuring cylinder and permitted to stand for 3h, 26 min, 6 sec. for sedimentation. The fine fraction

(< 2 µm) was removed and then placed in an electric vacuum oven at 50°C for 72 h to be dried. Then, it was put in a desiccator for subsequent experimentation. Scanning electron microscopy (SEM) is a powerful technique applied in micro imaging of a variety of surfaces. Based on SEM images of this nanoclay, it can be seen that the distance between the plates is Nano ("As shown in Figure 1a").

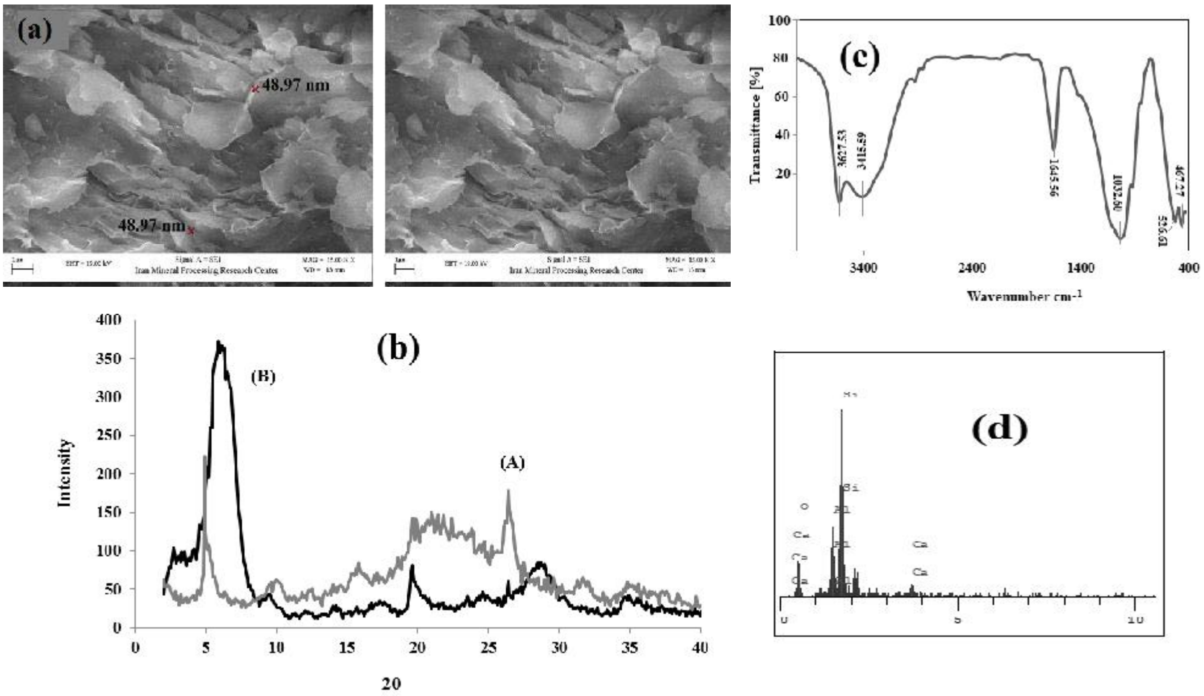


Figure 1. (a) SEM images (b) XRD patterns of the *Ghezeljeh* nanoclay are treated with ethylene glycol (A), Untreated (B). (c) FT-IR spectrum (d) EDX spectrum of untreated *Ghezeljeh* nanoclay.

Adsorption procedure

Adsorption experiments were carried out using batch method at room temperature. First, a 50 mL solution containing copper ions was transferred into an Erlenmeyer flask. Then, 10 mL of an appropriate buffer solution was added followed by 0.5 min of agitation. Next, 1.5 g of this nanoclay was added. The mixture was shaken for 10 min using a mechanical shaker. The liquid phase was separated from the solid phase via centrifugation at 8000 rpm for 5 min, the supernatant was decanted.

Desorption procedure

To elute the analytes adsorbed on to this nanoclay, 10 mL of 3 M HCl was added to the solid phase under stirring for 0.5 min, the suspension was allowed to stand for 20 min, and then, it was centrifuged at 3000 rpm for 10 min. The supernatant (10 mL) was collected to measure its copper ion concentration. To optimize the experimental conditions, these steps were repeated three times. The same method was applied to the blank solution.

Physicochemical characterization

XRD study

X-ray diffractograms were obtained for the 2θ angles ranging from 2 to 40° 2θ at room temperature. This nanoclay was treated with ethylene glycol, an organic compound which steadily intercalates itself into the lattice of the nanoclay. The structural properties of the clay were monitored before and after treatment with ethylene glycol [19]. The X-Ray diffraction analysis revealed that the nanoclay sample was chiefly composed of montmorillonite minerals ("As shown in Figure 1b").

FT-IR study

To prepare the clay sample for FT-IR spectroscopy, an electric vacuum oven was used to dry (at 50 °C for 6 h) and cool the clay. A FT-IR spectrum was recorded in the range of 400-4000 cm-1 using the KBr pellet technique. The KBr pellet was prepared by mixing the clay with KBr powder (at a ratio of around 1:100) and using a hydraulic press at a pressure of 10 tons. The FT-IR analysis, too, confirmed that the nanoclay was mainly composed of montmorillonite minerals ("As shown in Figure 1a") [19].

XRF and EDS study

XRF and EDS are the primary analytical tools for determining the elemental composition of trace evidence items. The chemical composition of bulk sediment is a function of mineralogy and mixing of minerals during sedimentological processes plays a primary role in controlling the bulk chemical composition. The chemical composition of this nanoclay was determined with XRF and EDS. "As shown in Figure 1d and Table1", demonstrates chemical composition of this nanoclay.

Table 1.XRF-analysis of the *Ghezeljeh* montmorillonite nanoclay.

Oxides	%
SiO_2	54.47
Al_2O_3	20.92
MgO	3.65
SO_3	0.32
K_2O	1.82
CaO	1.14
TiO_2	0.37
Fe_2O_3	3.13
PbO	0.16
SrO	0.10
ZrO_2	0.05
As_2O_3	0.02
L.O.I	13.86

Results and discussion

Prior to removing copper ions from real samples, standard solutions were subjected to preconcentration in order to optimize a number of operating parameters involved in the removal of copper ions from this nanoclay. The parameters were amount of adsorbent, eluent characteristics (type, concentration, and volume), pH of the buffer solutions, buffer type, adsorption temperature, shaking time, volume of the standard solution, and initial copper concentration (adsorption capacity). The role of desorption and centrifugation time were also studied. A summary of the main findings follows.

Effect of adsorbent dosage

Nine quantity levels of the nanoclay were studied: 0.1, 0.2, 0.3, 0.4, 0.5, 1, 1.5, 2, 2.5 g. The standard solution was 60 mL composing of 50 mL of doubly distilled water containing 2.5 mgL^{-1} of copper ions and 10 mL of buffer solution added at pH 7.5. The adsorption of the copper ions on to the nanoclay improved as the dosage of the nanoclay was increased. However, the adsorption declined at adsorbent dosages higher than 1.5 g. Reduction in the adsorption may be due to the fact that when the adsorbent amount is less than 1.5 g, the copper ions can simply come into contact with the adsorption sites, but when the adsorbent content exceeds 1.5 g, the number of such sites per unit mass decreases, because of aggregation and flocculation of adsorbent particles [20-22].

Effect of eluent characteristics

HCl and HNO_3 solutions were used at various concentrations (1-5 M) for the elution of copper ions adsorbed on to the nanoclay. The adsorbed ions were readily eluted (desorbed) from this nanoclay only when 10 mL of 3 M HCl was used.

Effect of pH of the buffer solutions

To study the effect of pH of the buffer solutions on desorption of copper ions from the nanoclay, pH was adjusted in the range of 4 to 10 at room temperature: pH 4-6 for acetate buffer, pH 7 for phosphate buffer, and pH 8-10 for ammonium buffer. Copper ions were optimally desorbed from the nanoclay at pH 7-8. For subsequent runs of the experiment, pH 7.5 was used as the optimum level for phosphate and ammonium buffer solutions.

Effect of buffer type

Two types of buffer solutions were compared at a concentration of 0.1 M at pH 7.5 in terms of their effect on copper adsorption: phosphate and ammonium. The ammonium buffer solution led to a higher level of copper ion adsorption.

Effect of adsorption temperature

To study the effect of temperature on copper ion adsorption, the temperature was varied in the range of 25-55 ºC. As it was found that increased temperature results in lower copper adsorption, room temperature was selected as the optimum value.

Effect of shaking time

To study the effect of shaking time (contact time), the adsorption of copper ions on to the nanoclay was measured after 5, 10, 20, 30, 40, 50 min of shaking the standard solution. The highest degree of adsorption was obtained after 10 min. This optimum value was used in the rest of experiments.

Effect of volume of the standard solution

To study the effect of the total volume of the standard solution (sample + buffer), on the adsorption of copper ions on to the nanoclay, seven quantities of 60, 120, 300, 420, 600, 900, and 1200 mL were investigated. It was found that recovery was over 95% at quantities of 60-1020 mL, but it declined to below 95% when the volume of the solution exceeded 1020 mL. Now, given that final solution volume to be measured by FAAS was 10 mL, therefore, the preconcentration factor was 102.

Effect of initial copper concentration

The adsorption capacity of an adsorbent is defined as the largest amount of metal adsorbed on to 1 g of the adsorbent [23]. In order to determine the adsorption capacity of this nanoclay, 1.5 g of the nanoclay was added to different standard solutions containing 0.153, 0.765, 1.53, 3.06, and 4.59 mg of copper ions. The adsorption capacity was calculated to be 0.65 mgg^{-1} (relative error smaller than ±5%).

Desorption time

Desorption time is defined as the length of time an eluent is in contact with the adsorbent containing metal ions. The desorption time in this work was studied by measuring recovery of copper ions from the nanoclay after 5, 10, 15, 20, and 25 min of contact between HCl and the nanoclay. Desorption time of 20 min was found to lead to the highest degree of desorption. This value was used in the remaining experiments.

Centrifugation time

To explore the effect of centrifugation on desorption of copper ions from the nanoclay, aliquots taken from the standard solutions after 20 min of desorption time were centrifuged for 2, 4, 6, 10, 16 min at a rotation speed of 3000 rpm. Highest recovery of copper ions was obtained at 10 min of centrifugation.

Interference from other ions

Given the fact that real samples usually contain more than one analyte, a variety of ions were added in salt form at milligram per liter levels to the standard solutions which already contained copper ions “As shown in Table 2”.

The purpose was to measure the degree to which each ion interfered with the recovery of copper ions from the nanoclay under the optimized conditions. Ions were considered to be interfering when they caused an error larger than ±5% in the recovery of copper ions. None of the added ions caused interference.

Table 2. The effect of additional metal ions on the determination of 2.5 µgmL^{-1} of Cu(II) ions (in optimum conditions; N=3).

Ion	Added as	Ion concentration (mgL^{-1})	Salt concentration (mgL^{-1})	Recovery%	RSD%
Na^+	NaCl	990	2500	97	1.1
Ag^{+a}	$AgNO_3$	2	3.5	97	2.9
Ca^{2+}	$CaCl_2$	1000	2500	95	2.6
Mg^{2+}	$MgSO_4$	250	2500	95	2.8
K^+	KCl	1300	2500	96	1.4
Zn^{2+}	$ZnSO_4$	400	1800	96	1.9
Fe^{3+}	$FeCl_3$	70	200	95	2.8
Mn^{2+}	$MnSO_4$	820	2500	96	1.9
Al^{3+}	$Al_2(SO_4)_3$	80	500	95	2.5
Ni^{2+}	$NiSO_4$	950	2500	96	2.2
Cd^{2+}	$Cd(NO_3)_2$	600	1670	96	2.5
Co^{2+}	$Co(NO_3)_2$	500	2500	96	2.2
Pb^{2+}	$Pb(NO_3)_2$	300	500	95	4.9
Cr^{3+}	$Cr(NO_3)_3$	85	650	95	3.9

[a] The presence of Cl^- ions in the ammonium chloride buffer solution causes Ag^+ ions to precipitate in the form of AgCl.

Figures of merit

The figures of merit for copper ions in the present study were calculated under optimal experimental conditions. The limit of detection (LOD) turned out to be 0.98 ngmL^{-1} based on three times the standard deviations of the blank solution (k = 3, n = 10). The value for limit of quantification (LOQ) 9.8 ngmL^{-1}, preconcentration factor 102, dynamic linear range (DLR) from 9.8 to 49 ngmL^{-1}, adsorption capacity of the nanoclay was 0.65 mgg^{-1}. On the whole, full recovery (100%) was obtained under the optimized conditions with standard solutions. The interaction between copper ions and the nanoclay was rapid, with the equilibrium batch process being attained in less than 10 min, meaning that the interaction was thermodynamically favorable.

Application to real samples

Separate food materials

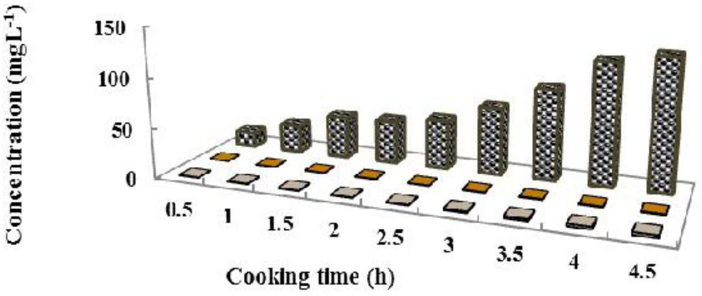
After the parameters involved in the adsorption and desorption of copper ions were optimized, the experimental method was separately applied to a variety of food materials in order to verify its efficiency in the determination and removal of copper ions in food samples, which were *Kura* or *filippi's bleak* (a kind of *Caspian* Sea fish), calf liver, potato, red bean, and sheep brain. Each sample was homogenized using an electrical mixer and then dried in an electrical oven at a temperature of 100°C for 24 h. The dried sample was homogenized again and was stored in polyethylene bottles for subsequent analysis. Samples were digested using wet digestion as described in literature [24]. One gram was taken from each food sample. Then, 16 milliliters of a mixture of HNO_3 and H_2O_2 (6:2) was added to each sample. The digestion vessel was heated on the hot plate up to 130°C for 4 h. The sample was allowed to cool. Then, 25 mL of doubly distilled water was added under stirring. The resulting solution was filtered through Whatman blue band filter paper. Afterwards, appropriate amounts of 4 M NaOH were added to adjust the pH level. The sample was then diluted using doubly distilled water until it was 50 mL. The digested food samples were poured into an Erlenmeyer flask. Ten mL of the buffer solution was added. After 0.5min of agitation, 1.5g of the clay was added. Subsequently, the preconcentration-extraction process was performed. The blank digestions were performed in the same way. The recovery of copper ions from the food samples under investigation was found to be in the range of about 70-91% at relative standard deviations of less than 5% "As shown in Table 3". This shows a decline in comparison with the standard solutions. However, it should be noted that the obtained percentage of recovery is still significant.

Table 3. Determination of Cu(II) ions in separate food samples (under optimum conditions; N=3).

Sample	Added (µg mL^{-1})	Found (µg mL^{-1})	Recovery%	RSD%
Kura (Fish)	-	1.23	-	3.1
	1.7	2.73	88.23	3.8
	3.4	3.96	80.29	4.5
	5.1	5.21	78.0	4.6
Liver (Calf)	-	6.60	-	3.2
	1.7	8.14	90.58	4.2
	3.4	9.56	87.06	3.8
	5.1	10.73	80.98	3.9
Potato	-	1.046	-	3.6
	1.7	2.39	79.41	4.5
	3.4	3.55	73.82	3.9
	5.1	4.62	70.19	4.7
Red Bean	-	1.06	-	4.5
	1.7	2.48	83.52	4.3
	3.4	3.78	80	4.8
	5.1	4.97	76.66	4.9
Brain (Sheep)	-	2.40	-	3.1
	1.7	3.95	91.17	3.6
	3.4	5.41	88.52	4.4
	5.1	6.53	80.98	4.1

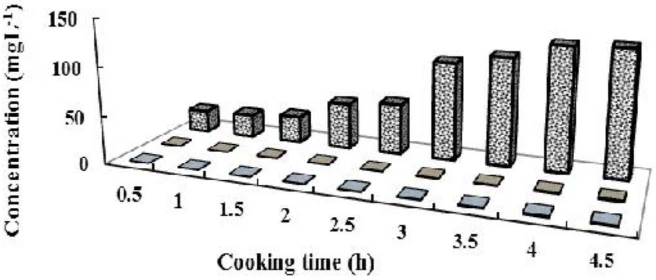
Stew samples

The method used in this investigation was also applied to two Iranian stews (*Fesenjan* and *Ghormeh Sabzi*) cooked in copper pots plated with tin. The goal was to identify and measure the amount of copper released into food from the pot. As a reference, these stews were also cooked in an aluminum pot (In Iran, foods are often cooked in aluminum pots). *Fesenjan* consists of walnuts, chicken, pomegranate paste, oil, salt, and spices. *Ghormeh Sabzi* is made up of vegetables, meat, red bean, tomato paste, oil, salt, and spices. Each stew was cooked in the two pots (copper and aluminum) under the same cooking conditions (type of ingredients, amount of ingredients, and heating temperature). The cooking time was 4.5 h for each sample; aliquots were taken every 0.5h. Thus, there were nine aliquots for each stew and each pot (totaling 36 aliquots). The aliquots were prepared for analysis using the same method described in Section 5.1. Stew samples were digested using the same digestion method described for separate food samples (Section 5.1 above). The only difference was that here 3g of each stew was used. For analysis, the digested stew samples were also treated in the same way as described in Section 5.1. “As shown in Figure 2 and Figure 3”, give the amount of copper ions released from the copper pot in the case of *Fesenjan* and *Ghormeh Sabzi,* respectively.



	0.5	1	1.5	2	2.5	3	3.5	4	4.5
□Cu	0.35	0.53	0.49	0.50	0.57	1.35	1.91	2.26	2.43
■Sn	0.1	0.2	0.3	0.4	0.4	0.4	0.6	0.6	0.7
▨Al	15	28	42	43	49	67	90	121	130

Figure 2. The amounts of copper, tin, and aluminum ions freed into the *Fesenjan* stew.



	0.5	1	1.5	2	2.5	3	3.5	4	4.5
□Cu	0.04	0.19	0.29	0.42	0.52	0.62	1.01	1.44	1.52
□Sn	0.3	0.4	0.6	0.6	0.6	0.7	1	1.5	1.8
▨Al	23	24	28	48	53	102	112	128	130

Figure 3. The amounts of copper, tin, and aluminum ions freed into the *Ghormeh Sabzi* stew.

It was necessary to determine the amount of aluminum and tin ions released into the stews from the aluminum pot and the tin plating of the copper pot. The determination was achieved using an ICP-AES spectrometer. The copper concentrations were found to be in the range of 0.35-2.43 mgL^{-1} and 0.04-1.52 mgL^{-1} in the *Fesenjan*, "As shown in Figure 2", and *Ghormeh Sabzi*, "As shown in Figure 3", samples, respectively. These results suggest that the amounts of released copper, tin and aluminum exceeded the tolerable daily intakes measured in $mgkg^{-1}$ of body weight per day: 1.5-3 for copper [4], 2 for tin [25], and 1 for aluminum (WHO, 1989, 1990) [15].

Comparison between this research and similar studies

This work used the preconcentration-extraction method for the removal of copper ions from food samples. "As shown in Table 4", compares this method and other studies using SPE procedures for the determination and removal of heavy metals in terms of type of analyte, adsorbent, LOD, and preconcentration factor. As can be seen, using this nanoclay resulted in a relatively low LOD, a comparatively high sample volume breakthrough, and a high preconcentration factor.

Table 4. Comparison between the method used in this research and similar studies using SPE procedures.

Analytes	Adsorbents	LOD[a]	P.F[b]	Studies
Cd, Cr, Cu, Pb, Zn	rice bran	0.56–1.85	100	[26]
Cu, Ni	Dowex Optipore SD-2 resin	1.03-1.90	50	[3]
Cd, Cr, Cu, Pb,Co,Ni	Celtek clay	0.25-0.73	32	[2]
Cu, Pb, Zn, Cd	SNP-loaded alumina	0.21-0.63	83	[27]
Cu, Co, Ni, Fe, Zn, Pb	Gold nanoparticle loaded in activated carbon (Au-NP-AC)	1.5-2.8	30	[28]
Fe, Cr(III), Cu, Cd, Pb, Ni	Nanosilicate	0.26–0.55	133	[29]
Pb, Fe, Cu	Functionalized activated carbon	0.16–0.41	-	[30]
Pb, Cd, Ni, Cu	Gallic acid-modified silica gel	0.58–0.92	200	[31]
Cu	*Ghezeljeh* montmorillonite nanoclay	0.98	102	This work

[a] LOD: limit of detection (μg L^{-1})

[b] PF: preconcentration

Conclusion

This research attempted to measure and remove copper ions released from the cooking pot into food samples using *Ghezeljeh* montmorillonite nanoclay as a natural adsorbent. The nanoclay was characterized using FT-IR, SEM, EDS, XRF and XRD. Based on SEM images of clay, it can be seen that the distance between the plates is Nano. For this purpose, first a number of relevant parameters were optimized using a standard solutions: amount of adsorbent, eluent characteristics (type, concentration, and volume), pH of the buffer solutions, buffer type, adsorption temperature, shaking time (contact time), volume of the standard solution, and initial copper concentration (adsorption capacity). Also, the role of desorption time and centrifugation time were explored. It was also found that additional metal ions in the aqueous solutions do not have a negative effect on copper recovery. The figures of merit were also calculated: LOD, 0.98 ngmL^{-1}; LOQ, 9.8 ngmL^{-1}; preconcentration factor, 102; DLR ranged from 9.8 to 49 ngmL^{-1}, and the adsorption capacity of the clay was 0.65 mgg^{-1}. In the optimized standard solutions, full recovery (100%) was obtained. At a later stage, the experimental method was applied to a variety of food materials under the optimized conditions in order to verify its efficiency. The preconcentration-extraction method was also applied to two Iranian stews (*Fesenjan* and *Ghormeh Sabzi*) cooked in copper pots plated with tin in order to measure the amount of copper ion released into food from the pot. The amounts of released copper and tin were found to be more than the tolerable daily intakes.

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