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Extraction of Some Divalent Metal Ions (Cadmium, Nickel and Lead) from Different Tea and Rice Samples Using *Ghezeljeh* Nanoclay (*Geleh-Sar-Shoor*) as a New Natural Sorbent

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This article presents the method of extraction-preconcentration of Lead, Cadmium, and Nickel ions from food samples using the *Ghezeljeh* montmorillonite nanoclay (*Geleh-Sar-Shoor*) as a new native adsorbent in batch single component systems. The extraction-preconcentration of heavy metals were carried out by applying the solid phase extraction (SPE) method followed by atomic absorption spectroscopy (AAS), and inductively coupled with plasma atomic emission spectroscopy (ICP-AES). The *Ghezeljeh* nanoclay was characterized by using Fourier transform infrared spectroscopy (FT-IR), Scanning electron microscopy-energy dispersive spectrometer operating (SEM-EDS), X-ray diffractometry (XRD), X-ray fluorescence (XRF), Cation Exchange Capacity (CEC) measurements, BET specific surface area and Zeta potential. According to BET theory, the specific surface areas of the *Ghezeljeh* nanoclay was calculated to be $19.8 \text{ m}^2 \text{ g}^{-1}$ whereas the cation exchange capacity was measured to be 150 meq/100 g. The results of XRD, XRF, FT-IR, Zeta potential and BET surface area of the nanoclay confirmed that montmorillonite was the dominant mineral phase. Based on SEM images of this clay, it can be seen that the distance between the plates is nm level. For all three ions, the detection and quantification limits, dynamic linear range, preconcentration factor, and adsorption capacity were obtained. The effect of various interfering ions was studied. The experimental method was successfully applied for the extraction of heavy metals in different tea and rice samples.

Keywords: Adsorption, Clay, Solid phase extraction, Lead, Cadmium, Nickel

INTRODUCTION

The pollution of the environment with toxic metals is a result of many human activities, such as mining and metallurgy, and the effects of these metals on the ecosystems are of large economic and public-health significance [1]. Nickel (Ni), lead (Pb), and cadmium (Cd) are among the toxic metals [2,3]. Because of the harmful effects of excessive intakes of heavy metals ions, it is necessary to determine their trace in water and food samples [4,5]. Solid-phase extraction (SPE) is an attractive enrichment-separation method for heavy metal ions. It is trouble-free, time- and price-saving that has high preconcentration factor, and can be directly used in

microliter volumes without any sample loss [6]. For the removal of various metal ions in natural waters and a variety of food samples, diverse conventional and nonconventional adsorbents have been reported, such as red mud [7], activated carbon [8], tree fern [9], sewage sludge [10], sawdust [11], silica [12], bone char [13], rice husk [14], bagasse fly ash [15], resin [16], polymetallic sea nodules [17], modified zeolite [18], spirogyra bioadsorbent [19], and *etc.* However, these extractors are often non-selective or very expensive. High specific surface area, chemical and mechanical stability, layered structure, high cation exchange capacity (CEC), tendency to hold water in the interlayer sites, and the presence of Bronsted and Lewis acidity have made clays exceptional adsorbent materials [3]. Dias *et al.* [20] used 2-mercaptobenzothiazole loaded on clays for SPE of Hg(II), Pb(II), Zn(II), Cd(II), Cu(II) and

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Mn(II) ions from an aqueous solution. Akcay and Kurtulmus [22] investigated the adsorption position for uranium on Turgutlu and Kula clays. Krikorian and Martin [22] used modified clays for the SPE of copper(II), cadmium(II), silver(I), nickel(II) and lead(II) ions. Mohamed *et al.* [23] used Aswan clay from Egypt for speciation and preconcentration of Cr(III) and Cr(VI) from synthetic solution and tannery wastewater. Soylak *et al.* [4] used Celtek clay as adsorbent for the separation-preconcentration of metal ions from environmental samples. Turan [24] investigated uptaking of trivalent chromium ions from aqueous solutions using kaolinite. Bhattacharyya and Gupta [6] investigated kinetic and thermodynamic removal of Cu(II) by natural and acid-activated clays. Now, let us give a brief review of the some previous researches into the issue of heavy metal ions in human food. Racz *et al.* [25] examined trace metals in culture mushrooms. Onianwa *et al.* [26] determined the concentrations of some trace metals in Nigerian dishes. Voegborlo *et al.* [27] investigated concentrations of Hg, Pb and Cd in canned Tuna fish. Doner and Akman [28] determined the presence of iron and zinc in bulgur (boiled pounded) wheat by graphite FAAS. Ranau *et al.* [29] studied the presence of aluminum in fish smeared with aluminum folio. Fernandez *et al.* [30] reported trace element determinations of the Spanish tea. Tuzen [31] determined the concentrations of heavy metals in some fish samples. Magalhães *et al.* [32] determined the concentrations of heavy metals in the leaves and tea of *Arrabidaea*. Narin *et al.* [33] determined the concentrations of heavy metals in black tea samples produced in Turkey. Bagheri *et al.* [34] described the preparation of new Pb(II)-imprinted polymeric particles for selective extraction and preconcentration of ultra-trace amounts of lead ions from vegetables, rice and fish samples.

In this study, a SPE technique was applied for the extraction of Ni²⁺, Pb²⁺ and Cd²⁺ ions by using the *Ghezlejh* montmorillonite nanoclay as a new natural adsorbent in the batch single component systems. The *Ghezlejh* 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). The *Ghezlejh* clay is characterized by using Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy-

Energy Dispersive Spectrometer Operating (SEM-EDS), X-ray Diffractometry (XRD), X-ray Fluorescence (XRF), Cation Exchange Capacity (CEC) measurements, BET specific surface area and Zeta potential. The results of XRD, XRF, FT-IR, Zeta potential, BET surface area and CEC of the *Ghezlejh* clay confirm that montmorillonite is the dominant mineral phase. Based on SEM images, it can be seen that the distance between the plates is at nm level. This adsorbent was prepared using the *Galehouse* method for the SPE of Cd²⁺, Ni²⁺ and Pb²⁺ ions. The effect of adsorbent amount, eluent characteristics, pH and type of buffer solutions, shaking time, sample volume, and concentration of the sample solution were investigated to optimize the methodology. Finally, the presented method was successfully applied for the extraction of Cd²⁺, Ni²⁺ and Pb²⁺ ions in different food samples.

EXPERIMENTAL

Reagents and Materials

All the reagents were purchased from the German company of Merck: acids, bases, hydrogen peroxide, sodium acetate, nitrate salts of copper, silver, lead, chromium, nickel, cobalt, cadmium, sulfate salts of aluminum, manganese, zinc, magnesium, chloride salts of sodium, potassium, iron, calcium and ammonium. All the chemicals were of the highest purity, and needed no further purification.

The standard solutions of elements were produced by diluting a stock solution of 1000 mg l⁻¹ of the specified element using doubly distilled water. A citrate-citric acid buffer solution was prepared using 0.1 M citric acid solution at pH 2-3. The 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. The phosphate buffer solution was prepared using 0.1 M phosphoric acid at pH 7. The 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 *Ghezlejh* montmorillonite nanoclay (adsorbent) was collected from *Ghezlejh*, a village 18 km west of the city of *Tafresh* in Iran. To the best of our knowledge, *Ghezlejh* montmorillonite nanoclay (*Geleh-Sar-Shoor*) has

not been yet used as adsorbent for the extraction-preconcentration of heavy metals. Only Soleimani's researching group in Imam Khomeini International University (IKIU) has used *Geleh-Sar-Shoor* for the extraction of metal ions. The different samples of raw rice and tea (black and green) used in the experiments were all purchased from the local markets in *Qazvin*, 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 data were obtained using an Ital Structures diffractometer (GNR, Novara, Italy), with Cu K_{α} radiation (40 kV/30 mA, $\lambda = 1.542 \text{ \AA}$). Fourier Transform Infrared study was carried out using Tensor Bruker MIR-T27 (Germany) having a standard mid-IR DTGS detector. Due to decreasing laboratory and analysis costs, the quantitative measurements of Ni^{2+} , Pb^{2+} and Cd^{2+} ions in the standard solutions and the optimization of operating parameters involved in the extraction, 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. But, the analysis of food samples and figures of merit experiments were performed with a Varian 735-ES inductively coupled plasma atomic emission spectrometry (ICP-AES), (Mulgrave, Australia). Philips X-ray fluorescence of the sample has been studied using XRF Analysis Instruments (Philips Magix Pro, Netherlands). A scanning electron microscope (LEO 1450 VP, Thornwood, N.Y., USA) with variable pressure secondary electron detector and energy dispersive spectrometer operating at 30 kV (Oxford INCA software, High Wycombe, U.K.) were used for SEM-EDX analysis.

Clay

Clays are hydrous aluminum silicates which are classified as either 1:1 or 2:1 clay minerals. Montmorillonite is dioctahedral clay of the smectite group and is composed

of alumino-silicate layers. The silica tetrahedra (T) (Si^{4+} in tetrahedral coordination with O^{2-}) and alumina octahedral (O) (Al^{3+} in octahedral coordination with O^{2-}) are interconnected (*via* the sharing of O^{2-} at polyhedral corners and edges) in such a way that a sheet of alumina octahedral is sandwiched between two sheets of silica tetrahedral. Thus, the composition is T-O-T (2:1) [35-44].

Preparation of the Adsorbent

This adsorbent was prepared by using the *Galehouse* method [45-47]. The native *Ghezeljeh* montmorillonite nanoclay (*Geleh-Sar-Shoor*) was first treated with 0.1 M of acetic acid to eliminate carbonates, and then with 30% H_2O_2 to remove 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 allowed to stand for 3 h, 26 min, 6 s for sedimentation. The fine fraction ($< 2 \mu\text{m}$) was removed and then placed in an electric vacuum oven at $50 \text{ }^\circ\text{C}$ for 72 h to be dried. Then, it was placed in a desiccator for subsequent experiment.

SOLID PHASE EXTRACTION PROCEDURE

Adsorption Step

Adsorption experiments were carried out by using a batch method at room temperature. First, a 50 ml solution containing nickel or lead or cadmium 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, 0.5 g of the *Ghezeljeh* montmorillonite nanoclay was added. The mixture was shaken for 10 min using a mechanical shaker. It is necessary to know that in water samples with low ionic strength, the stability of colloids is high and coagulation occurs slowly (months to years), however, in waters with high ionic strength (appropriate buffer solutions) the stability of suspended colloids is reduced extensively and rapid coagulation occurs. Consequently, the liquid phase was separated from the solid phase *via* centrifugation at 3500 rpm for 5 min. The supernatant was decanted facilely (Fig. 1).

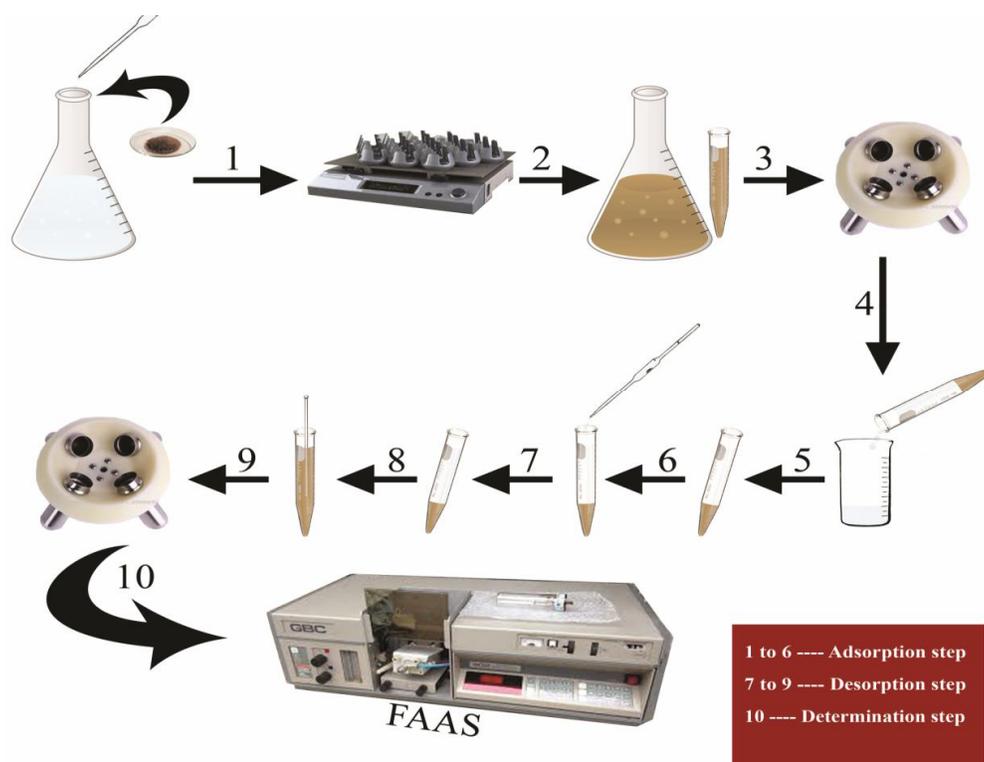


Fig. 1. Schematic diagram of the Adsorption, desorption and determination procedure.

Desorption Step

To elute the analytes adsorbed onto the *Ghezeljeh* nanoclay, 10 ml of 3 M HCl solution was added to the solid phase under stirring for 0.5 min, then, the suspension was allowed to stand for 10 min, and it was centrifuged at 3500 rpm for 30 min. The supernatant (10 ml) was collected to measure its nickel or lead or cadmium ions concentration. To optimize the experimental conditions, these steps were repeated three times. The same method was applied to the blank solution (Fig. 1).

PHYSIOCHEMICAL CHARACTERIZATION

The Scanning Electron Microscope is a powerful technique applied in micro imaging of a variety of surfaces. The clay sample was coated with Au under vacuum in argon atmosphere, and solid morphology, particle size and texture on surface clay were determined (Fig. 2a). Based on the SEM images of the *Ghezeljeh* montmorillonite nanoclay, the distance between the plates is at nm level.

X-ray diffractograms were obtained for the 2θ angles ranging from 2° - 40° 2θ at room temperature. The *Ghezeljeh* montmorillonite nanoclay was treated with ethylene glycol, an organic compound which steadily intercalates itself into the lattice of the clay. The structural properties of this nanoclay were monitored before and after treatment with ethylene glycol. The X-Ray diffraction analysis revealed that this clay sample was chiefly composed of montmorillonite minerals (Fig. 2b) [36,48]. Generally, montmorillonitic minerals show two types of XRD reflections: 1) basal reflections which vary with the state of hydration and 2) non-basal reflections (hk bands) characteristic of the montmorillonite mineral which are independent of the interlayer hydration. The montmorillonite sample under study showed a basal reflection at 5.8 2θ (15.24 \AA) indicating the formation of two layers of molecular water in the interlamellar space. The characteristic of bands are found at 19.5 (4.40 \AA), 35.2 2θ (2.55 \AA) [49].

To prepare the nanoclay sample for the Fourier

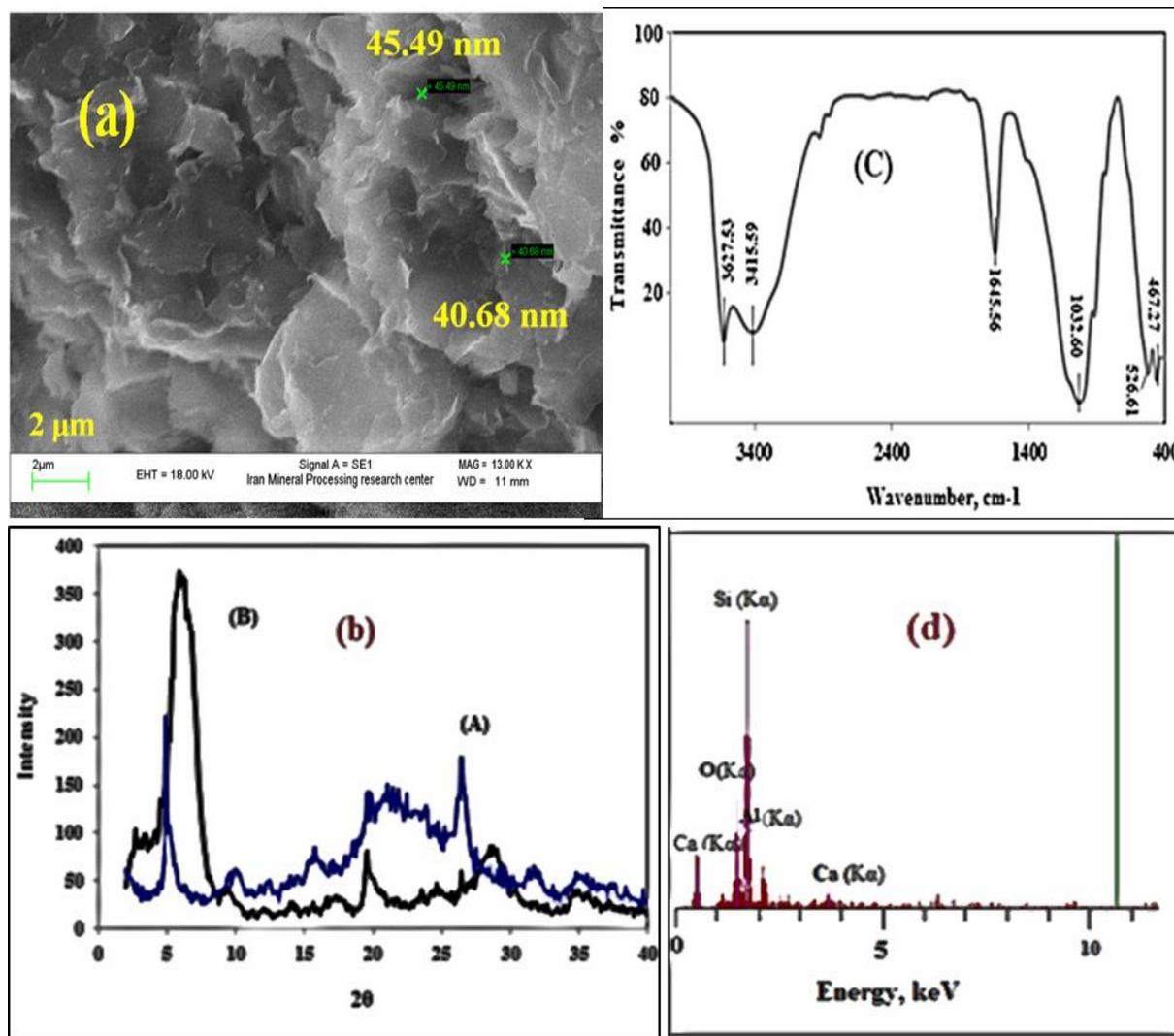


Fig. 2. (a) SEM images (b) XRD patterns of the *Ghezlejh* nanoclay are treated with ethylene glycol (A), Untreated (B). (c) FT-IR spectrum (d) EDX spectrum of the untreated *Ghezlejh* nanoclay.

Transform Infrared 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. FT-IR spectrum of the untreated *Ghezlejh* nanoclay (Fig. 2c) shows the bands at 3626 cm^{-1} in OH stretching region, which are assigned to hydroxyl groups

coordinated to octahedral cations (Al^{3+} cations). The most intensive band at 1035 cm^{-1} is attributed to Si-O in-plane stretching and 529 cm^{-1} is due to Si-O bending vibrations. The shoulder at 1113 cm^{-1} shows Si-O out-of-plane stretching vibration. The broad bands at 3440 cm^{-1} and 1639 cm^{-1} are the stretching and bending vibrations for the hydroxyl groups of water molecules present in the clay [36]. Montmorillonite had two characteristic FT-IR regions [50], (i) 3500-3750 cm^{-1} (due to the surface structural OH groups

of layered aluminosilicates and adsorbed water) and (ii) 400-1150 cm^{-1} (due to lattice vibrations). Consequently, the FT-IR analysis confirmed that the *Ghezeljeh* montmorillonite nanoclay was mainly composed of montmorillonite minerals [36].

X-ray fluorescence analysis and energy dispersive X-ray are the primary analytical tools for determining the elemental composition of trace evidence items [51]. The technique of XRF spectroscopy is analogous to EDS in that an X-ray spectrum is attained, representing an elemental fingerprint of the sample. The differences between the EDS and XRF data are largely due to the methodology characteristic of each technique. XRF gives the overall composition of a sample, instead, the EDS data are an average of several local compositions which are dependent on the positions at which the analysis is performed. One of the advantages of XRF is the ability to detect major, minor, and trace levels of an element, whereas EDS is limited to major and minor elemental concentrations. The chemical composition of the *Ghezeljeh* nanoclay was determined with XRF and EDS (Fig. 2d). Results of XRF analysis: 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; Loss-on-ignition corrections (L.O.I.): 13.86.

The cation exchange capacity is the number of equivalents of exchangeable charge per mass of the clay, equivalent with the layer charge [52]. The CEC of the *Ghezeljeh* montmorillonite nanoclay was measured with 0.01 M Cu-triethylenetetramine [36,53]. The CEC value of 160.0 meq/100 g for the *Ghezeljeh* montmorillonite nanoclay was found, and the very large CEC value agrees well with the CEC values for Montmorillonite reported in the literature [54].

The specific surface area (S_{BET}), pore volume and pore radius of the *Ghezeljeh* montmorillonite nanoclay were distinguished by the Brunauer-Emmett-Teller (BET) method and derived from N_2 adsorption isotherms measured at liquid nitrogen temperature (at 77 K) using a Belsorp mini II instrument (BelJapan, Japan). Moisture and gases on the solid surface or penetrated in the open pores were removed by heating under vacuum at 100 °C for 12 h prior to the surface area measurements. The *Ghezeljeh* montmorillonite

nanoclay possesses a specific surface area of 90.916 $\text{m}^2 \text{g}^{-1}$, pore volume of 0.147 $\text{cm}^3 \text{g}^{-1}$ and pore radius of 4.8 nm [55,45].

The zeta potential of the *Ghezeljeh* nanoclay was obtained from electrophoretic mobility measurements at 21.31 °C, with Zetameter apparatus (ZetaCAD instruments). The zeta potential measured at a natural pH of 5.64 is -25.970 mV and comparable to zeta potentials of montmorillonite (-21.2 mV) [56].

RESULTS AND DISCUSSION

Prior to removing nickel, lead, and cadmium ions from natural samples, standard solutions were subjected to extraction-preconcentration method to optimize a number of operating parameters involved in the extraction of metal ions. The parameters were amount of adsorbent, eluent characteristics (type, concentration, and volume), pH of the buffer solutions, buffer type, contact time, volume of the standard solutions, and initial nickel, lead, and cadmium ions concentration (adsorption capacity). The role of desorption and centrifugation times were also studied. A summary of the main findings follows.

Effect of pH of the Buffer Solutions

To study the effect of pH of the buffer solutions on the adsorption of Ni^{2+} , Cd^{2+} and Pb^{2+} ions onto the *Ghezeljeh* montmorillonite nanoclay, pH was adjusted in the range of 2-10 at room temperature by using buffer solutions given in section reagents and solutions. Ni^{2+} , Cd^{2+} and Pb^{2+} ions were optimally adsorbed on the nanoclay at pH 5-6. For subsequent runs of the experiment, pH 5.5 was used as the optimum pH level for acetate buffer solution. The results are shown in Fig. 3a. Clays are known to have a negative surface charge in solution, as pH changes, surface charge as well changes, and the adsorption of charged species is affected. At low pH values, there are excess of H_3O^+ ions in solution, a competition exists between the positively charged hydrogen ions and metal ions for the available adsorption sites on the negatively charged clay surface. However at pH values higher than 6, Ni^{2+} , Cd^{2+} and Pb^{2+} ions are being precipitated from the solution in the form of hydroxides.

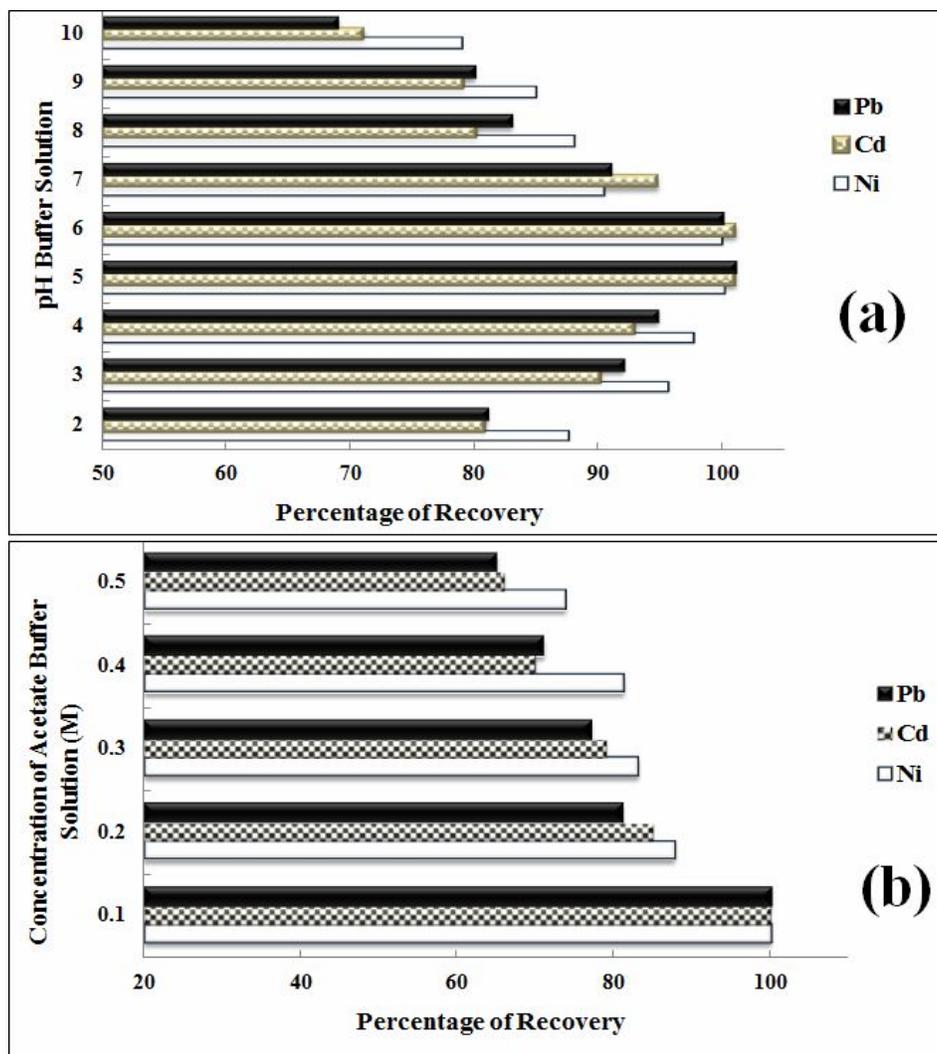


Fig. 3. Effect of the (a) pH buffer solution (b) the concentration of acetate buffer solution on the recoveries of analytes (a 50 ml solution containing 20 μg of Ni^{2+} or 4.5 μg of Cd^{2+} or 62.5 μg Pb^{2+} ion plus 10 ml buffer solution; adsorption temperature: 25 $^{\circ}\text{C}$; eluent: 10 ml 3 M HCl; amount of nanoclay: 0.5 g, N = 3).

Effect of Buffer Solution Concentration

To investigate the effect of acetate buffer solution concentration for the adsorption of Ni^{2+} , Cd^{2+} and Pb^{2+} ions onto the nanoclay, the concentration of acetate buffer solutions in the ranges of 0.1-0.5 M at pH 5.5 at room temperature are changed. Figure 3b shows that the maximum percentage of recovery is obtained at 0.1 M.

Effect of Adsorbent Amount

Eight quantity levels of the nanoclay were studied: 0.1, 0.2, 0.3, 0.4, 0.5, 1, 1.5 and 2 g. The standard solution was 60 ml composed of 50 ml of doubly distilled water containing 20 μg of Ni^{2+} , 4.5 μg of Cd^{2+} , and 62.5 μg Pb^{2+} ions, and 10 ml of buffer solution. In order to elute the analytes adsorbed onto the *Ghezeli* nanoclay, 10 ml of 3 M HCl solution was used. Content analysis was applied by flame atomic absorption spectrometry. The adsorption of

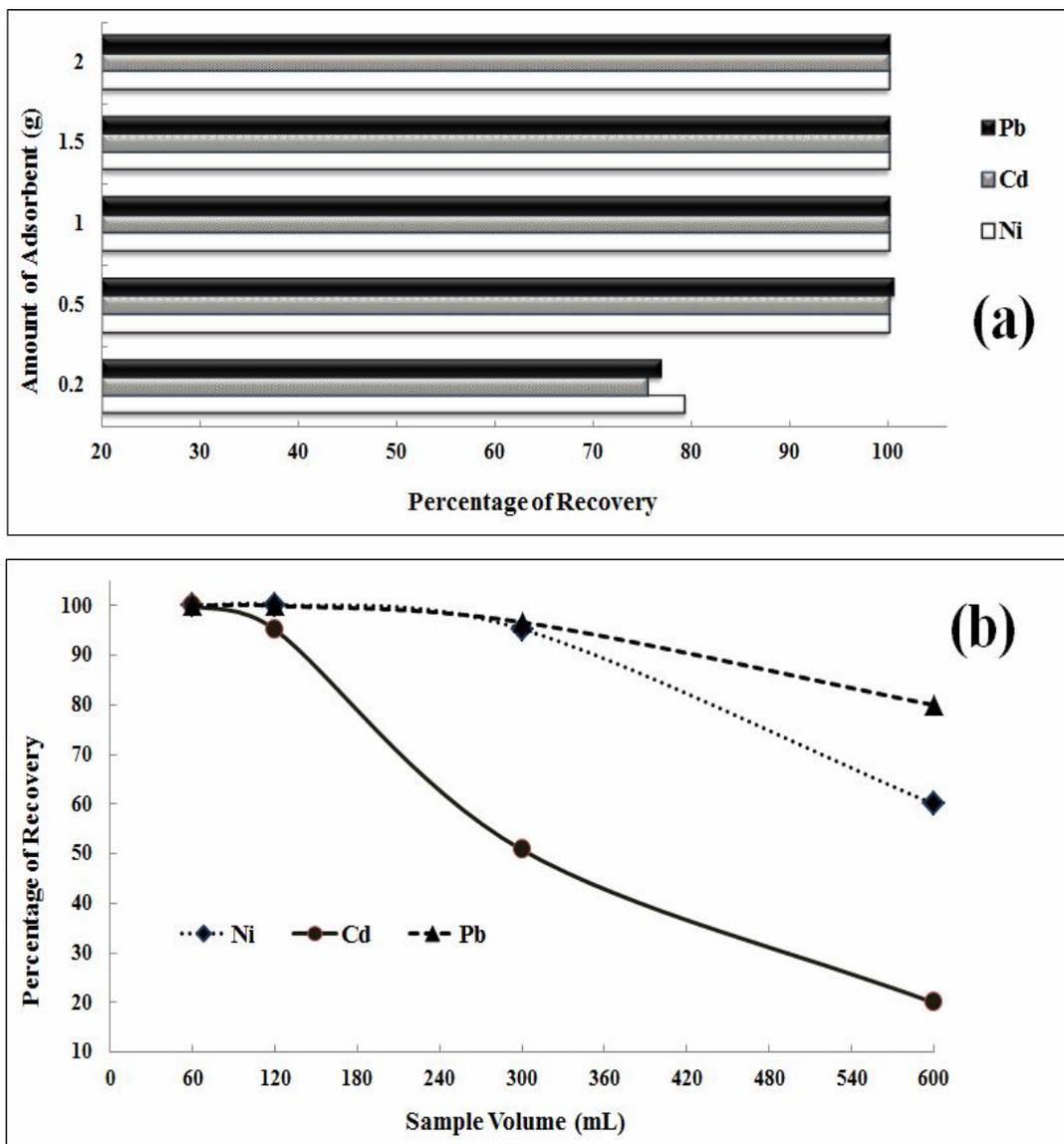


Fig. 4. Effect of the (a) amount of nanoclay (a 50 ml solution containing 20 μg of Ni^{2+} or 4.5 μg of Cd^{2+} or 62.5 μg Pb^{2+} ion plus 10 ml acetate buffer solution pH 5.5; eluent: 10 ml 3 M HCl; adsorption temperature: 25 $^{\circ}\text{C}$; N = 3) (b) sample volume on the recoveries of analytes (containing 20 μg of Ni^{2+} or 4.5 μg of Cd^{2+} or 62.5 μg Pb^{2+} ion); eluent: 10 ml 3 M HCl; acetate buffer solution pH 5.5; amount of nanoclay: 0.5 g; adsorption temperature: 25 $^{\circ}\text{C}$; N = 3).

the metal ions onto the nanoclay enhanced as the amount of the nanoclay increased, after than 0.5 g of the nanoclay remained basically unchanged. For subsequent runs of the experiment, 0.5 g of the nanoclay was used as the optimum amount of the adsorbent level [3,6,57,58] (Fig. 4a).

Effect of Eluent Characteristics

To obtain suitable eluent, HCl and HNO_3 solutions were used at various concentrations (1-5 M) with varying volumes (5-15 ml) for the elution of Ni^{2+} , Cd^{2+} and Pb^{2+} ions adsorbed on to the nanoclay. The adsorbed ions were

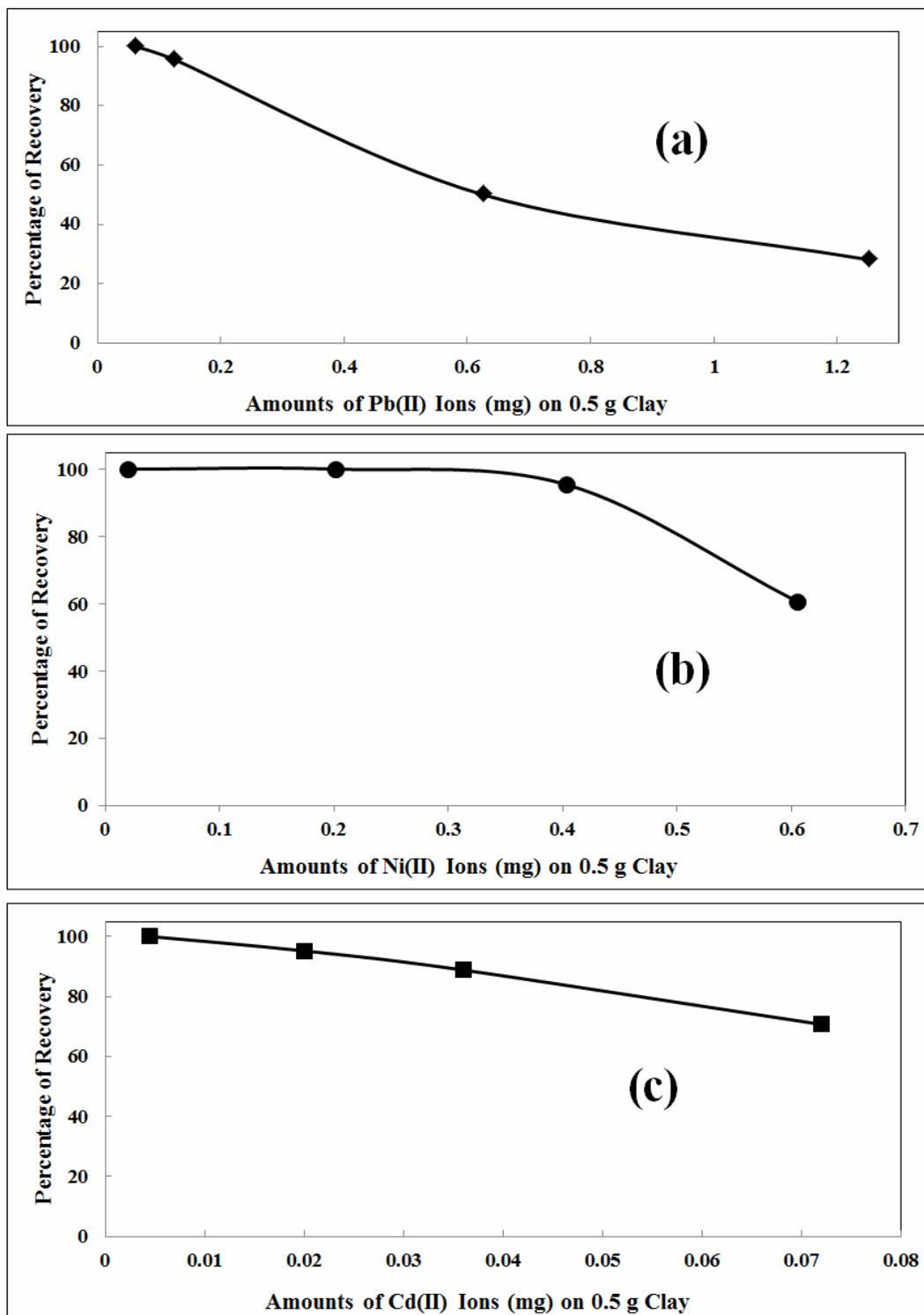


Fig. 5. Effect of the initial metal ion concentration (adsorption capacity) on the recoveries of analytes (50 ml sample volume plus 10 ml acetate buffer solution pH 5.5; eluent: 10 ml 3 M HCl; amount of nanoclay: 0.5 g; adsorption temperature: 25 °C; N = 3).

readily eluted (desorbed) from the *Ghezleleh* nanoclay only when 10 ml of 3 M HCl solution was used. The recovery values increase with increasing acid concentration. At higher concentration of acid (> 3 M), the recovery values decrease. The reason is that most of the octahedral sheet cations like Al, Mg and Fe were dissolved by increasing acid concentration [59]. These elements in atomic absorption air/acetylene flame interfere with this heavy metal, therefore, the absorption intensity decreases. The same procedure was applied to the blank solution.

Effect of Adsorption Time

To study the effect of shaking time (contact time), the adsorption of Ni^{2+} , Cd^{2+} and Pb^{2+} ions on to the *Ghezleleh* nanoclay was measured after 5, 10, 15, 20 and 30 min of shaking the standard solutions. It was observed that after 5 min, the adsorption was completed. Consequently metal-clay interactions reached equilibrium in less than 10 min. It indicated that, the adsorption sites on the *Ghezleleh* nanoclay minerals were rapidly covered by Ni^{2+} , Cd^{2+} and Pb^{2+} ions. On the basis of the results, a 10 min of adsorption time (shaking time) was found appropriate for maximum adsorption. This optimum value was used in the rest of experiments.

Effect of Standard Solution Volume

To study the effect of the standard solution volume (sample + buffer), on the adsorption of Ni^{2+} , Cd^{2+} and Pb^{2+} ions onto the nanoclay, four quantities of 60, 120, 300 and 600 ml (containing 20 μg of Ni^{2+} or 4.5 μg of Cd^{2+} or 62.5 μg Pb^{2+} ions) were investigated. Because of the low concentrations of trace metals in natural samples, these analytes should be taken into smaller volumes for high preconcentration factor (P.F.) by using sample solutions with large volumes. It was found that recovery was over 95% at quantitative up to 300, 300 and 120 ml of sample volume for Ni^{2+} , Pb^{2+} and Cd^{2+} ions, respectively, however it declined to below 95% when the volume of the solution exceeded 300, 300 and 120 ml. Now, since the final solution volume measured by FAAS was 10 ml, the preconcentration factors of 30, 30 and 12 were obtained for Ni^{2+} , Pb^{2+} and Cd^{2+} ions, respectively. The results are recorded in Fig. 4b.

Effect of Initial Metal Ions Concentration

The adsorption capacity of an adsorbent is defined as the largest amount of metal adsorbed on to 1 g of the adsorbent [3]. In order to determine the adsorption capacity of the *Ghezleleh* nanoclay, 0.5 g of the nanoclay was added to different standard solutions containing 0.02018, 0.2018, 0.4036 and 0.6054 mg of Ni^{2+} ions; 0.0625, 0.1251, 0.6256, and 1.251 mg of Pb^{2+} ions; 0.0045, 0.020, 0.036, and 0.072 mg of Cd^{2+} ions (Fig. 5). The adsorption capacities of the *Ghezleleh* nanoclay were calculated to be 0.806, 0.250 and 0.040 mg g^{-1} for Ni^{2+} , Pb^{2+} and Cd^{2+} ions, respectively (relative error less than $\pm 5\%$). At lower concentrations, a large number of adsorption sites on the nanoclay are available to the metal ions and this condition changes with increasing metal ion concentration and the competition for adsorption sites becomes difficult.

Effect of Desorption Time

Desorption time is defined as the length of time that an eluent is in contact with the adsorbent containing metal ions. The desorption time in this work was studied by measuring the recovery of Ni^{2+} , Pb^{2+} and Cd^{2+} ions from the nanoclay after 5, 10, 15, 20 and 30 min of contact between HCl solution and the *Ghezleleh* nanoclay. In desorption time of 10 min, the highest degree of desorption was found, consequently, this value was used in the remaining experiments.

Effect of Centrifugation Time

To explore the effect of centrifugation time on the desorption of Ni^{2+} , Pb^{2+} and Cd^{2+} ions from the *Ghezleleh* nanoclay, aliquots taken from the standard solutions after 10 min of desorption time were centrifuged for 5, 10, 15, 20 and 30 min at a rotation speed of 3500 rpm. Highest recovery of metal ions was obtained for 30 min of centrifugation.

Interference Studies

Given the fact that natural samples containing more than one analyte, a variety of ions were added in salt form at milligram per liter levels to the standard solution that each of them contained Ni^{2+} ion, Pb^{2+} ion and Cd^{2+} ion (Tables

Table 1. The Effect of Additional Metal Ions on the Extraction of Ni²⁺ Ion (a 50 ml Solution Containing 20 µg of Ni²⁺ Ion Plus 10 ml Acetate Buffer Solution pH 5.5; 10 ml 3 M HCl Eluent; 0.5 g Nanoclay, 25 °C; N = 3)

Ion	Added as	Ion concentration (mg l ⁻¹)	Salt concentration (mg l ⁻¹)	Recovery (%)	RSD (%)
Na ⁺	NaCl	630	1600	95	1.9
Ca ²⁺	CaCl ₂	36	100	95	3.1
Mg ²⁺	MgSO ₄	15	150	95	2.1
K ⁺	KCl	419	800	95	1.9
Zn ²⁺	ZnSO ₄	250	1100	95	2.5
Fe ³⁺	FeCl ₃	35	100	95	4.4
Mn ²⁺	MnSO ₄	310	950	95	2.5
Al ³⁺	Al ₂ (SO ₄) ₃	55	700	95	3.9
Cd ²⁺	Cd(NO ₃) ₂	328	900	95	3.8
Co ²⁺	Co(NO ₃) ₂	365	1800	95	4.3
Pb ²⁺	Pb(NO ₃) ₂	566	905	95	4.3
Cr ³⁺	Cr(NO ₃) ₃	110	850	95	2.6
Cu ²⁺	Cu(NO ₃) ₂	215	810	95	2.8

Table 2. The Effect of Additional Metal Ions on the Extraction of Cd²⁺ Ion (a 50 ml Solution Containing 4.5 µg of Cd²⁺ Plus 10 ml Acetate Buffer Solution pH 5.5; 10 ml 3 M HCl Eluent; 0.5 g Nanoclay, 25 °C; N = 3)

Ion	Added as	Ion concentration (mg l ⁻¹)	Salt concentration (mg l ⁻¹)	Recovery (%)	RSD (%)
Na ⁺	NaCl	670	1700	95	1.6
Ca ²⁺	CaCl ₂	29	80	95	4.2
Mg ²⁺	MgSO ₄	10	100	95	2.9
K ⁺	KCl	523	1000	95	2.6
Zn ²⁺	ZnSO ₄	228	1000	95	2.1
Fe ³⁺	FeCl ₃	76	220	95	4.1
Mn ²⁺	MnSO ₄	228	700	95	3.3
Al ³⁺	Al ₂ (SO ₄) ₃	40	500	95	3.9
Ni ²⁺	NiSO ₄	163	800	95	2.7
Co ²⁺	Co(NO ₃) ₂	375	1850	95	2.2
Pb ²⁺	Pb(NO ₃) ₂	87	140	95	2.6
Cr ³⁺	Cr(NO ₃) ₃	130	1000	95	3.3
Cu ²⁺	Cu(NO ₃) ₂	235	890	95	3.1

Table 3. The Effect of Additional Metal Ions on the Extraction of Pb²⁺ Ion (a 50 ml Solution Containing 62.5 µg Pb²⁺ Ion Plus 10 ml Acetate Buffer Solution pH 5.5; 10 ml 3 M HCl Eluent; 0.5 g Nanoclay, 25 °C; N = 3)

Ion	Added as	Ion concentration (mg l ⁻¹)	Salt concentration (mg l ⁻¹)	Recovery (%)	RSD (%)
Na ⁺	NaCl	512	1300	95	2.4
Ca ²⁺	CaCl ₂	25	68	95	2.9
Mg ²⁺	MgSO ₄	21	210	95	3.4
K ⁺	KCl	728	1200	95	4.2
Zn ²⁺	ZnSO ₄	300	1300	95	2.9
Fe ³⁺	FeCl ₃	62	180	95	3.8
Mn ²⁺	MnSO ₄	319	980	95	4.4
Al ³⁺	Al ₂ (SO ₄) ₃	16	200	95	4.6
Ni ²⁺	NiSO ₄	203	1000	95	4.1
Cd ²⁺	Cd(NO ₃) ₂	437	1200	95	4.7
Co ²⁺	Co(NO ₃) ₂	405	2000	95	3.1
Cr ³⁺	Cr(NO ₃) ₃	85	650	95	3.7
Cu ²⁺	Cu(NO ₃) ₂	264	1000	95	4.3

1-3). The purpose was to measure the degree to which each ion interfered with the recovery of Ni²⁺, Pb²⁺ and Cd²⁺ ions from the *Ghezljeh* nanoclay under the optimized conditions. Ions were considered to be interfering when they caused an error larger than ±5% in the recovery of Ni²⁺, Pb²⁺ and Cd²⁺ ions. None of the added ions caused interference.

Figures of Merit

The figures of merit experiments for Ni²⁺, Pb²⁺ and Cd²⁺ ions in the present study were calculated under optimal experimental conditions in natural sample matrixes with a Varian 735-ES inductively coupled plasma atomic emission spectrometry after application of the solid phase extraction procedure to blank solutions. Considering the preconcentration factors of 30, 30 and 12 for Ni²⁺, Pb²⁺, and Cd²⁺ ions, respectively, the limit of detection (LOD) based

on three times the standard deviations of the blank solution (k = 3, n = 10) turned out to be 0.5 ng ml⁻¹ for Ni²⁺, Pb²⁺ and Cd²⁺ ions. The value for the limit of quantification (LOQ) was 1.6 ng ml⁻¹ for Ni²⁺, Pb²⁺ and Cd²⁺ ions. The dynamic linear range (DLR) for Ni²⁺ and Pb²⁺ were from 1.6 ng ml⁻¹ to 13.3 µg ml⁻¹ and for Cd²⁺ from 1.6 ng ml⁻¹ to 8.34 µg ml⁻¹. The adsorption capacities of the *Ghezljeh* nanoclay were calculated to be 0.806, 0.250 and 0.040 mg g⁻¹ for Ni²⁺, Pb²⁺, and Cd²⁺ ions, respectively (relative error smaller than ±5%).

APPLICATION

Natural Samples (Rice and Tea)

After the parameters involved in the adsorption and desorption of Ni²⁺, Pb²⁺ and Cd²⁺ ions were optimized, the method used in this research was separately applied to seven

Table 4. Extraction of Ni²⁺ Ion in Rice Samples (Optimum Conditions; N = 3)

Sample	Added ($\mu\text{g ml}^{-1}$)	Found ($\mu\text{g ml}^{-1}$)	Recovery (%)	RSD (%)
<i>Argentinian rice</i>	-	< LOQ	-	1.1
	1.009	1.000	99.1	2.2
	2.018	1.900	94.0	3.1
	3.027	2.500	82.5	3.2
<i>Hashemi rice</i>	-	< LOQ	-	0.9
	1.009	0.980	97.1	2.4
	2.018	1.670	82.7	3.3
	3.027	2.390	78.9	3.2
<i>Sadri rice</i>	-	< LOQ	-	0.9
	1.009	0.940	93.1	2.8
	2.018	1.760	87.2	2.8
	3.027	2.400	79.2	3.2
<i>Shirodi rice</i>	-	< LOQ	-	1.5
	1.009	0.860	85.2	3.3
	2.018	1.60	79.2	3.1
	3.027	2.30	76.0	2.8
<i>Neda rice</i>	-	< LOQ	-	1.4
	1.009	0.880	87.2	2.6
	2.018	1.560	77.3	3.2
	3.027	2.300	76.0	3.3
<i>Kamalol Molki rice</i>	-	< LOQ	-	1.6
	1.009	1.000	99.1	1.9
	2.018	1.980	98.1	2.4
	3.027	2.780	91.8	3.7

< LOQ: lower than quantification limit.

Table 5. Extraction of Cd²⁺ Ion in Rice Samples (Optimum Conditions; N = 3)

Sample	Added ($\mu\text{g ml}^{-1}$)	Found ($\mu\text{g ml}^{-1}$)	Recovery (%)	RSD (%)
<i>Argentinian rice</i>	-	< LOQ	-	1.9
	0.225	0.220	97.7	2.4
	0.450	0.410	91.1	4.1
	0.900	0.810	90.0	3.9
<i>Hashemi rice</i>	-	< LOQ	-	3.2
	0.225	0.210	93.3	2.9
	0.450	0.420	93.3	3.0
	0.900	0.800	88.8	3.3
<i>Sadri rice</i>	-	< LOQ	-	2.6
	0.225	0.200	88.8	2.5
	0.450	0.380	84.4	3.6
	0.900	0.750	83.3	3.7
<i>Shirodi rice</i>	-	< LOQ	-	2.5
	0.225	0.190	84.4	2.3
	0.450	0.370	82.2	4.0
	0.900	0.700	77.7	3.8
<i>Neda rice</i>	-	< LOQ	-	2.0
	0.225	0.210	93.3	2.6
	0.450	0.400	88.8	3.4
	0.900	0.770	85.5	3.6
<i>Kamalol Molki rice</i>	-	< LOQ	-	1.9
	0.225	0.220	97.7	2.8
	0.450	0.430	95.5	3.3
	0.900	0.830	92.2	3.8

Table 6. Extraction of Pb²⁺ Ion in Rice Samples (Optimum Conditions; N = 3)

Sample	Added ($\mu\text{g ml}^{-1}$)	Found ($\mu\text{g ml}^{-1}$)	Recovery (%)	RSD (%)
<i>Argentinian rice</i>	-	0.200	-	2.1
	0.782	0.960	97.2	2.8
	1.564	1.700	96.0	3.0
	3.128	3.100	92.7	4.0
<i>Hashemi rice</i>	-	< LOQ	-	1.2
	0.782	0.710	90.80	2.2
	1.564	1.400	89.0	3.1
	3.128	2.700	86.3	3.9
<i>Sadri rice</i>	-	< LOQ	-	3.6
	0.782	0.730	93.3	2.5
	1.564	1.400	89.5	3.9
	3.128	2.800	89.5	4.5
<i>Shirodi rice</i>	-	< LOQ	-	2.5
	0.782	0.750	96.0	3.0
	1.564	1.450	92.7	3.8
	3.128	2.900	92.7	4.7
<i>Neda rice</i>	-	< LOQ	-	3.1
	0.782	0.710	90.8	4.0
	1.564	1.300	83.1	4.0
	3.128	2.500	79.9	4.1
<i>Kamalol Molki rice</i>	-	0.050	-	2.9
	0.782	0.760	90.8	3.3
	1.564	1.400	86.3	4.1
	3.128	2.450	76.7	4.5

Table 7. Extraction of Ni²⁺ Ion in Tea Samples (Optimum Conditions; N = 3)

Sample	Added ($\mu\text{g ml}^{-1}$)	Found ($\mu\text{g ml}^{-1}$)	Recovery (%)	RSD (%)
<i>Jasmine</i> green tea bag	-	< LOQ	-	1.1
	1.009	1.000	99.1	2.9
	2.018	2.000	99.1	3.5
	3.027	2.800	92.5	4.8
<i>Golestan</i> black tea	-	< LOQ	-	2.2
	1.009	0.870	86.2	3.2
	2.018	1.700	84.2	3.9
	3.027	2.500	82.5	4.6
<i>Ceylon Special</i> black tea bag	-	< LOQ	-	3.6
	1.009	0.900	89.2	4.5
	2.018	1.800	89.2	3.9
	3.027	2.600	85.9	4.7
<i>Dimeh</i> black tea	-	< LOQ	-	2.5
	1.009	0.810	80.3	4.0
	2.018	1.600	79.3	3.8
	3.027	2.400	79.3	4.6
<i>Doghazal</i> black tea	-	< LOQ	-	2.1
	1.009	0.910	90.2	3.6
	2.018	1.800	89.2	4.0
	3.027	2.500	82.6	4.1
<i>Gulabi Barooti</i> black tea	-	< LOQ	-	2.1
	1.009	1.000	99.1	2.2
	2.018	1.900	94.1	3.2
	3.027	2.750	90.8	4.4
Noncommercial Green tea	-	0.080	-	1.9
	1.009	1.050	96.1	3.3
	2.018	2.020	96.1	3.8
	3.027	2.800	89.8	4.2

Table 8. Extraction of Pb²⁺ Ion in Tea Samples (Optimum Conditions; N = 3)

Sample	Added ($\mu\text{g ml}^{-1}$)	Found ($\mu\text{g ml}^{-1}$)	Recovery (%)	RSD (%)
<i>Jasmine</i> green tea bag	-	< LOQ	-	1.1
	0.782	0.710	90.8	2.8
	1.564	1.400	89.5	4.0
	3.128	2.800	89.5	4.3
<i>Golestan</i> black tea	-	< LOQ	-	2.1
	0.782	0.730	93.3	4.0
	1.564	1.450	92.7	3.8
	3.128	2.850	91.1	4.5
<i>Ceylon Special</i> black tea bag	-	0.060	-	1.6
	0.782	0.790	93.3	2.5
	1.564	1.500	91.8	3.8
	3.128	2.800	87.6	4.1
<i>Dimeh</i> black tea	-	< LOQ	-	4.5
	0.782	0.770	98.5	4.3
	1.564	1.500	95.9	4.8
	3.128	2.860	91.4	4.5
<i>Doghazal</i> black tea	-	< LOQ	-	3.1
	0.782	0.750	95.9	3.6
	1.564	1.470	93.9	4.7
	3.128	2.800	89.5	4.5
<i>Gulabi Barooti</i> black tea	-	< LOQ	-	1.9
	0.782	0.710	90.8	2.9
	1.564	1.300	83.1	3.5
	3.128	2.550	81.5	4.3
Noncommercial Green tea	-	0.120	-	2.1
	0.782	0.870	96.0	3.3
	1.564	1.600	94.6	4.1
	3.128	3.000	92.0	4.7

Table 9. Extraction of Cd²⁺ Ion in Tea Samples (Optimum Conditions; N = 3)

Sample	Added ($\mu\text{g ml}^{-1}$)	Found ($\mu\text{g ml}^{-1}$)	Recovery (%)	RSD (%)
<i>Jasmine</i> green tea bag	-	< LOQ	-	1.1
	0.225	0.210	93.3	2.8
	0.450	0.400	88.8	4.0
	0.900	0.800	88.8	4.3
<i>Golestan</i> black tea	-	< LOQ	-	2.2
	0.225	0.220	97.7	3.2
	0.450	0.410	91.1	3.8
	0.900	0.780	86.6	4.5
<i>Ceylon Special</i> black tea bag	-	< LOQ	-	2.3
	0.225	0.190	84.5	3.5
	0.450	0.380	84.4	3.9
	0.900	0.760	84.4	4.5
<i>Dimeh</i> black tea	-	< LOQ	-	1.5
	0.225	0.220	97.7	3.3
	0.450	0.430	95.5	4.4
	0.900	0.810	90.0	4.0
<i>Doghazal</i> black tea	-	< LOQ	-	3.1
	0.225	0.210	93.3	3.6
	0.450	0.410	91.1	4.4
	0.900	0.790	87.7	4.4
<i>Gulabi Barooti</i> black tea	-	< LOQ	-	1.8
	0.225	0.220	97.7	2.9
	0.450	0.430	95.5	4.2
	0.900	0.800	88.8	4.4
Noncommercial Green tea	-	< LOQ	-	1.4
	0.225	0.200	88.8	1.9
	0.450	0.400	88.8	2.7
	0.900	0.800	88.8	2.8

Table 10. 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	[63]
Cu, Ni	DowexOptipore SD-2 resin	1.03-1.90	50	[5]
Cd, Cr, Cu, Pb,Co,Ni	Celtek clay	0.25-0.73	32	[4]
Cu, Pb, Zn, Cd	SNP-loaded alumina	0.21-0.63	83	[64]
Cu, Co, Ni, Fe, Zn, Pb	Gold nanoparticle loaded in activated carbon (Au-NP-AC)	1.5-2.8	30	[65]
Fe, Cr(III), Cu, Cd, Pb, Ni	Nanosilicate	0.26-0.55	133	[66]
Pb, Fe, Cu	Functionalized activated carbon	0.16-0.41	-	[67]
Pb, Cd, Ni, Cu	Gallic acid-modified silica gel	0.58-0.92	200	[68]
Pb, Cd, Ni, Cu, Co	Carboxylic acid (COOH) bonded to silica gel	2.1-17.5	80,120	[69]
Ni, Pb, Cd	<i>Ghezeljeh</i> montmorillonite nanoclay	0.5,0.5,0.5	30,30,12	This work

^aLOD: limit of detection ($\mu\text{g l}^{-1}$), ^bPF: preconcentration factor.

commercial and noncommercial type black and green tea samples, and six type rice samples. All of them were procured from local markets and hypermarkets in Iran.

Tea samples: *Jasmine* green tea bag, *Gilan* area, north of Iran; *Golestan* black tea, India; *Erfan Ceylon Special* black tea bag, flavored with bergamot, Sri Lanka; *Dimeh* black tea, *Langrood* area, north of Iran; *Doghazal* black tea, without flavored, Sri Lanka; *Gulabi Barooti* black tea, India; Noncommercial type green tea, north of Iran.

Rice samples: *Kamalol Molki* rice, India; *Neda* rice, north of Iran; *Shirodi* rice, north of Iran; *Sadri* rice, north of Iran; *Hashemi* rice, north of Iran and rice from Argentina. Samples dried in an electrical oven at a temperature of 80 °C for 4 h. The dried sample was stored in polyethylene bottles for subsequent analysis. Samples were digested using wet digestion according to procedure given in literatures [33,60,61]. A portion (1 g) of sample dried was

taken from each food sample. Then, 16 milliliters of a mixture of HNO₃ and H₂O₂ (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 solution were added to adjust the pH level. The samples were then diluted using doubly distilled water until 50 ml. The digested food samples were poured into an Erlenmeyer flask, and 10 ml of the buffer solution was added. After 0.5 min of agitation, 0.5 g of the *Ghezeljeh* montmorillonite nanoclay was added. Subsequently, the extraction-preconcentration process was performed. The blank digestions were performed in the same way. The contents of Ni²⁺, Pb²⁺ and Cd²⁺ ions were determined by a Varian 735-ES inductively coupled plasma atomic emission

spectrometry. The results are reported in Tables 4-9. A decline in the recoveries of Ni²⁺, Pb²⁺ and Cd²⁺ ions were observed, however, the percentage of the recovery was still significant with low relative standard deviations (less than 5%). The results revealed that the level of the metals in the rice and tea samples were within the recommended ranges, and below the permissible levels recommended by the United States Environmental Protection Agency and World Health Organization (USEPA and WHO). Therefore, the consumption of these rice and tea samples may not constitute health hazards to humans at the time of the study. The maximum permissible doses for an adult are 3 mg l⁻¹ Pb²⁺, 5 mg l⁻¹ Ni²⁺ and 0.5 mg l⁻¹ Cd²⁺ per week, but the recommended doses are only one-fifth of those quantities [31,62].

Comparison between this Research and Similar Studies

Table 10 compares this method and other studies by using SPE procedure for the extraction of the heavy metals in terms of type of analyte, adsorbent, the limit of detection (LOD), and preconcentration factor. As can be seen, using the *Ghezalje* montmorillonite nanoclay resulted in a relatively low LOD.

CONCLUSIONS

This research attempted for the extraction-preconcentration of Ni²⁺, Cd²⁺ and Pb²⁺ ions from food samples by using the *Ghezalje* montmorillonite nanoclay as a new natural adsorbent. The *Ghezalje* clay was characterized by using Fourier transform infrared spectroscopy, scanning electron microscopy, X-ray diffractometry, X-ray fluorescence, BET surface area, Zeta potential and CEC measurements. The results of XRD, XRF, BET surface area, FT-IR and Zeta potential of the *Ghezalje* clay confirmed that montmorillonite was the dominant mineral phase. Based on SEM images, it can be seen that the distance between the plates is at nm level. This adsorbent was prepared using the *Galehouse* method and then a number of extraction effective parameters were optimized. The additional metal ions in the aqueous solution already containing Ni²⁺ or Cd²⁺ or Pb²⁺ ions generally did not have a negative effect on metal ion recovery. For all

three ions, the limits of detection and quantification 0.5 µg l⁻¹ and 1.6 µg l⁻¹ were obtained respectively. The dynamic linear range (DLR) for Ni²⁺ and Pb²⁺ were from 1.6 ng ml⁻¹ to 13.3 µg ml⁻¹, and for Cd²⁺ ion from 1.6 ng ml⁻¹ to 8.34 µg ml⁻¹, preconcentration factor 30, 30 and 12 for Ni²⁺, Pb²⁺ and Cd²⁺ ions, and the adsorption capacity of the nanoclay 0.806, 0.250 and 0.040 mg g⁻¹ for Ni²⁺, Pb²⁺ and Cd²⁺ ions were obtained, respectively. Finally, the experimental method was successfully applied for the extraction of Ni²⁺, Pb²⁺ and Cd²⁺ ions in diverse tea and rice samples, under the optimized conditions. The interactions between Ni²⁺, Pb²⁺ and Cd²⁺ ions with this *Ghezalje* nanoclay were rapid and an equilibrium batch process was obtained in less than 30 min. Therefore, the extraction of heavy metal ions by using the *Ghezalje* montmorillonite nanoclay was efficient, reproducible, rapid, and reliable in diverse natural samples.

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