

ORIGINAL RESEARCH PAPER

## Trace Cd(II), Pb(II) and Ni(II) ions extraction and preconcentration from different water samples by using *Ghezeljeh* montmorillonite nanoclay as a natural new adsorbent

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### ABSTRACT

This investigate presents the extraction-preconcentration of Lead, Cadmium, and Nickel ions from water samples using *Ghezeljeh* montmorillonite nanoclay or "*Geleh-Sar-Shoor*" (means head-washing clay) as a natural and native new adsorbent in batch single element systems. The *Ghezeljeh* clay is categorized 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, Surface property valuation ( $S_{BET}$ ) by the BET method from nitrogen adsorption isotherms and Zeta potential. According to BET theory, the specific surface area of *Ghezeljeh* nanoclay was computed as  $19.8 \text{ m}^2 \text{ g}^{-1}$  whereas the cation exchange capacity was determined as 150 meq ( $100 \text{ g}^{-1}$ ). The results of XRD, FT-IR, XRF, zeta potential, BET surface area and CEC of the *Ghezeljeh* clay 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 nm level. For all three ions, the limit of detection, the limit of quantification, dynamic linear range, preconcentration factor, and the adsorption capacity were obtained. The result of several interfering ions was considered. The *Ghezeljeh* nanoclay as a new adsorbent and experimental method were effectively used for the extraction of heavy metals (Lead, Cadmium, and Nickel) in a variety of real water samples.

**Keywords:** Water, Nanoclay, Solid phase extraction, Lead, Cadmium, Nickel.

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## INTRODUCTION

The elimination of toxic heavy metals from aqueous environmental samples has received significant attentions in latest years due to gathering in living tissues, and consequent bio exaggeration in the food chain improving their poisonousness [1]. Nickel (Ni), lead (Pb), and cadmium (Cd) are among the toxic heavy metals [2,3]. Because of the damaging properties of extreme intakes of heavy metals ions, it is required to define their trace in water and food samples [4,5]. Solid-phase extraction (SPE) is an attractive enrichment-separation

manner for heavy metal ions. It is trouble-free, high preconcentration factor, time- and price-saving, and can be straight used in microliter volumes without any sample loss [6]. For the subtraction of numerous metal ions in natural waters and a variety of food samples, different conventional and nonconventional adsorbents have been stated, 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.

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However, these extractors are frequently non-selective or exceedingly expensive. High specific surface area, chemical and mechanical stability, layered structure, high cation exchange capacity (CEC), affinity to hold water in the interlayer sites, and the existence 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 Mn(II) from an aqueous solution. Akcay and Kurtulmus [21] examined the adsorption position for uranium on Turgutlu and Kula clays. Krikorian and Martin [22] used adjusted 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. Tuzen et al. [4] used Celtek clay as adsorbent for the separation-preconcentration of metal ions from environmental samples. Turan [24] studied the uptake of trivalent chromium ions from aqueous solutions using kaolinite. Bhattacharyya and Gupta [6] explored kinetic and thermodynamic exclusion of Cu(II) by natural and acid-activated clays.

In this study, a solid phase extraction (SPE) in batch equilibrium procedure was used to extract Ni<sup>2+</sup>, Pb<sup>2+</sup>, and Cd<sup>2+</sup> ions using *Ghezeljeh* montmorillonite nanoclay as a native new adsorbent in batch single component systems. *Ghezeljeh* montmorillonite nanoclay is exceptionally cheap; its price is \$ 0.1/kg. There is no requirement to recover the clay due to its low price. The industrial water organization by using clay materials as an adsorbent is reasonable according to its low price. Only Soleimani and Hassanzadeh in the Imam Khomeini International University (IKIU) have used *Geleh-Sar-Shoor* for the extraction of metal ions [25-28]. It is interesting to mention that the *Ghezeljeh* nanoclay (*Geleh-Sar-Shoor*) was used in olden Persia to clean the body, hair, and also to bathe dead bodies prior to the funeral ("*Geleh-Sar-Shoor*" means head-washing clay). The *Ghezeljeh* clay was characterized using FT-IR, SEM-EDS, XRF, XRD, BET surface area, cation exchange capacity (CEC) and Zeta potential. The adsorbent was readied using the *Galehouse* method for the SPE of Cd<sup>2+</sup>, Ni<sup>2+</sup>, and Pb<sup>2+</sup> ions. The influence of the quantity of adsorbent, eluent characteristics, pH and type of buffer solutions, shaking time, desorption time, centrifugation time, sample volume, and concentration of the sample solution

were examined to optimize the procedure. Finally, the presented technique was effectively used for the extraction of Cd<sup>2+</sup>, Ni<sup>2+</sup>, and Pb<sup>2+</sup> ions in real different water samples.

### Clay

Clays are hydrous aluminum silicates which are categorized as either 1:1 or 2:1 clay minerals. The sheets in these clays are held together by weak Van Der Waals forces creating it easy for other chemicals to enter the interlayer region. Many 2:1 clay minerals have permanent negative charge due to isomorphous substitution of aluminum(III) for silicon(IV) in the silica layer or magnesium(II) for aluminum(III) in the alumina layer [29]. Montmorillonite is dioctahedral clay of the smectite group and is composed of aluminosilicate layers. The Silica Tetrahedral (T) (Si<sup>4+</sup> in tetrahedral coordination with O<sup>2-</sup>) and alumina octahedral (O) (Al<sup>3+</sup> in octahedral coordination with O<sup>2-</sup>) are interconnected (via the sharing of O<sup>2-</sup> at polyhedral corners and edges) in such a way that a sheet of alumina octahedral is sandwiched between two sheets of silica tetrahedral. Consequently, the composition is T-O-T (2:1) [30]. Most of the surface charges on montmorillonite are produced by isomorphous substitution or non-ideal octahedral occupancy. These permanent negative charges are distributed along the mineral basal surfaces and are well-adjusted by absorbing aqueous cations, such as Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>. These cations can be exchanged with other cations in solution and the exchange reactions are non-specific, stoichiometric and encompass the creation of surface outer-sphere complexes. In montmorillonite, the edge sites account for a much lesser fraction of the exchange capacity. The adsorption of metals to these sites includes the creation of surface inner-sphere complexes analogous to the interaction of these metals with the surfaces of oxide minerals [31,32]. Substitution of metal cations by clay minerals is organized by restrictions such as charge characteristics of the clay [33,34]. The exchange manners exhibited depend on several factors, like the physicochemical features of solid and cation (such as ionic radius, charge size, hard-soft acid-base properties, hydration volume and hydration enthalpy of cation), existence of challenging ions, temperature, ionic strength and investigational situations containing time of reaction, concentration of ions, and pH of the medium [33-44].

## MATERIALS AND METHODS

### Reagents and solutions

All the reagents were bought from the German company of Merck: acids, bases, hydrogen peroxide, sodium acetate, sodium citrate, 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. Since the reagents were of the highest purity, they were applied without any additional purification.

The element standard solutions were prepared by diluting a stock solution of 1000 mg L<sup>-1</sup> of the specified element using doubly distilled water. A citrate-citric acid buffer solution was readied using 0.1 M citric acid solution at pH 2-3. Acetate buffer solution was used 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 organized 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 was collected from *Ghezeljeh*, a village 18 km west of the city of Tafresh in Iran. The different real water samples used in the experiments were collected from Caspian Sea (Iran), Karun River (inside and outside the city of Ahvaz, Iran), Persian Gulf (Iran), well water (Herat, Afghanistan), Haryrood River (Afghanistan), and tap water (Herat, Afghanistan).

### Instrumentation

A model 420A digital Orion pH meter (Gemini, the Netherlands) equipped with a combined glass electrode was used for pH adjustments. An ultrasonic water bath (Bandelin, Berlin, Germany) was applied to disperse and disaggregate the *Ghezeljeh* montmorillonite nanoclay. Agitation of the system was carried out on a mechanical shaker (Flask shaker SF1 Scientific model, STUART, Britain). X-Ray Diffraction (XRD) data were attained using an Ital Structures diffractometer (GNR, Novara, Italy), with Cu K $\alpha$  radiation (40 kV/30 mA,  $\lambda = 1.542 \text{ \AA}$ ). 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 Ni(II), Pb(II), and Cd(II) ions in the standard solutions, a

GBC 902 flame atomic absorption spectrometry (FAAS), (Dandenong, Victoria, Australia 3175) with deuterium background corrector and an air-acetylene flame was applied. The working conditions in the FAAS spectrometer were adjusted according to the standard guidelines of the manufacturer. But, the analysis of real water samples were achieved with a Varian 735-ES inductively coupled plasma atomic emission spectrometry (ICP-AES), (Mulgrave, Australia). X-ray fluorescence (XRF) of the sample has been investigated 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 applied for SEM-EDS analysis. Zeta potential measurements were carried out on a Zetameter ZetaCAD (CAD Instruments, France). The specific surface areas were studied with the BET way using a Belsorp mini II instrument (BelJapan, Japan).

### Preparation of the adsorbent

The adsorbent was organized using the *Galehouse* way [45]. Natural *Ghezeljeh* montmorillonite nanoclay was initially handled with 0.1 M of acetic acid to remove carbonates, and then with 30% H<sub>2</sub>O<sub>2</sub> to disregard mineral and organic impurities. The *Ghezeljeh* montmorillonite nanoclay was carefully washed with doubly distilled water to reject traces of acetic acid and hydrogen peroxide. The treated nanoclay was spread and disaggregated in doubly distilled water through an ultrasonic water bath. The resultant suspension was moved to a measuring cylinder and allowed to stand for 3 h, 26 min, 6 sec for sedimentation. The fine part (< 2  $\mu\text{m}$ ) was removed and then located in an electric vacuum oven at 50°C for 72 h to be dehydrated. Then, it was placed in a desiccator for following experimentation [25-28].

### Solid phase extraction (SPE) procedure

#### Adsorption step

Adsorption tests were carried out using batch technique at room temperature. First, a 50 mL solution containing nickel or lead or cadmium ions were moved into an Erlenmeyer flask. Then, 10 mL of a proper buffer solution was added followed by 0.5 min of agitation. Then, 0.5 g of the *Ghezeljeh* montmorillonite nanoclay was added. The mixture was shaken for 10 min by means of a mechanical

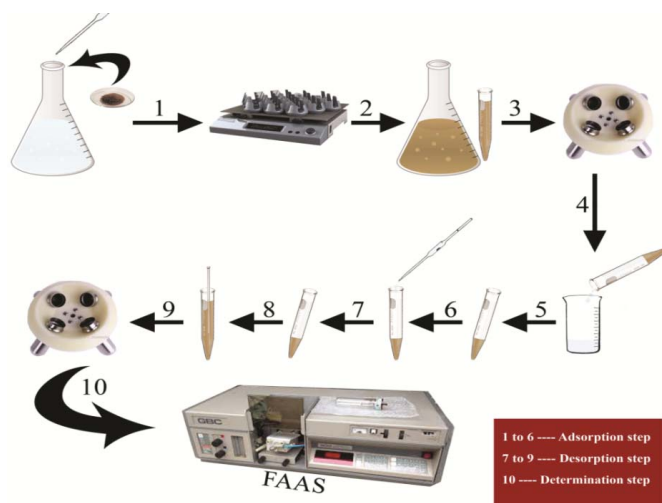


Fig. 1: Schematic diagram of the Adsorption, desorption and determination procedure.

shaker. The liquid part was disconnected from the solid part via centrifugation at 3500 rpm for 5 min. The supernatant was decanted (Fig. 1).

#### Desorption step

To elute the analytes adsorbed on to the *Ghezjeljeh* montmorillonite nanoclay, 10 mL of 3M HCl solution was added to the solid phase under stirring for 0.5 min. Then, the suspension was permitted to stand for 10 min and was centrifuged at 3500 rpm for 30 min. The supernatant (10 mL) was collected to determine its nickel or lead or cadmium ions concentration. To optimize the experimental conditions, these steps were repeated three times. The equivalent process was used to the blank solution (Fig. 1).

#### Physicochemical characterization

##### SEM study

Scanning Electron Microscopy (SEM) is a powerful technique used in micro imaging of a diversity of surfaces. The *Ghezjeljeh* montmorillonite nanoclay sample was covered with Au under vacuum in argon atmosphere (Fig. 2a). Based on SEM images of the *Ghezjeljeh* montmorillonite clay, it can be seen that the distance between the plates is nm level.

##### XRD study

X-ray diffractograms were attained for the  $2\theta$  angles ranging from  $2^\circ$  to  $40^\circ 2\theta$  at room temperature. The *Ghezjeljeh* nanoclay was treated with ethylene glycol, an organic compound which steadily intercalates itself into the lattice of the clay. The

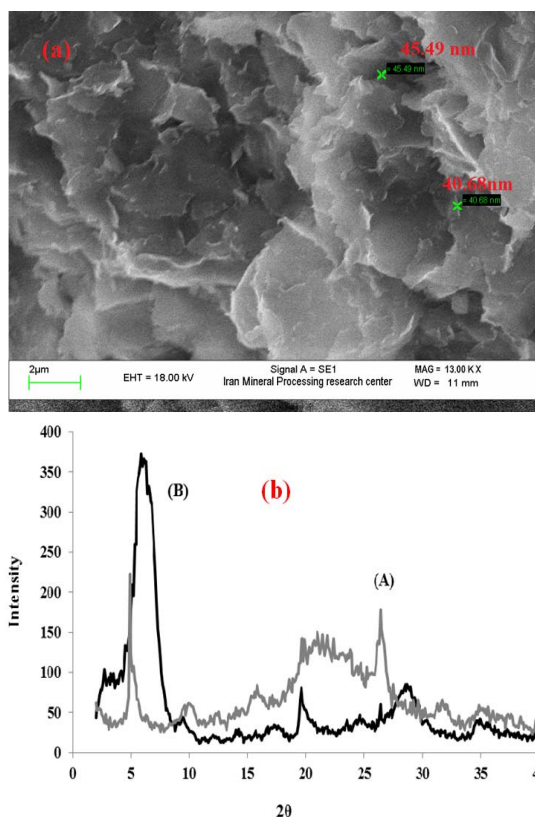


Fig. 2: (a) SEM image (b) The XRD patterns of *Ghezjeljeh* montmorillonite nanoclay (A) treated with ethylene glycol (B) Untreated.

structural properties of the *Ghezjeljeh* nanoclay were observed before and after treatment with ethylene glycol. The X-Ray diffraction analysis exposed that the *Ghezjeljeh* nanoclay sample was mainly composed of montmorillonite minerals (Fig. 2b) [30].

### FT-IR study

To prepare the *Ghezeljeh* montmorillonite nanoclay sample for FT-IR spectroscopy, an electric vacuum oven was applied to dehydrated (at 50°C for 6 h) and cool the nanoclay in a desiccator. A FT-IR spectrum was recorded in the range of 400–4000  $\text{cm}^{-1}$  using the KBr pellet technique. FT-IR spectrum of untreated *Ghezeljeh* montmorillonite nanoclay (Fig. 3a) displays the bands at 3626  $\text{cm}^{-1}$  in OH stretching region, which are assigned to hydroxyl groups coordinated to octahedral cations ( $\text{Al}^{3+}$  cations). The maximum intensive band at 1035  $\text{cm}^{-1}$  is attributed to Si-O in-plane stretching and 529  $\text{cm}^{-1}$  is due to Si-O bending vibrations. The shoulder at 1113  $\text{cm}^{-1}$  shows Si-O out-of-plane stretching vibration. The broad bands at 3440  $\text{cm}^{-1}$  and 1639  $\text{cm}^{-1}$  are the stretching and bending vibrations for the hydroxyl groups of water molecules present in the clay. Montmorillonite had two characteristic FT-IR regions [45], (i) 3500–3750  $\text{cm}^{-1}$  (due to the surface structural OH groups of layered aluminosilicates and adsorbed water) and (ii) 400–1150  $\text{cm}^{-1}$  (due to lattice vibrations). Subsequently, the FT-IR analysis confirmed that *Ghezeljeh* nanoclay was chiefly composed of montmorillonite minerals [30].

### XRF and EDS studies

The technique of XRF spectroscopy is similar to EDS in that an X-ray spectrum is achieved which signifies an elemental fingerprint of the sample.

The main difference between XRF and EDS is the excitation energy. XRF applies an X-ray beam to yield characteristic X-rays, while EDS applies an electron beam. XRF gives the total composition of a sample. Instead, the EDS data are an average of some local compositions which are dependent on the locations at which the analysis is achieved. One of the advantages of XRF is the capability to identify major, minor, and trace levels of an element, however, EDS is restricted to major and minor elemental concentrations. Subsequently, the detection limit for XRF is about 10 part per million (p.p.m.) and EDS is about 1% [47–50]. The chemical composition of the *Ghezeljeh* montmorillonite nanoclay was determined with XRF and EDS. Table 1 and Fig. 3b proves chemical composition of this clay [51].

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

Oxides	%
$\text{SiO}_2$	54.47
$\text{Al}_2\text{O}_3$	20.92
MgO	3.65
$\text{SO}_3$	0.32
$\text{K}_2\text{O}$	1.82
CaO	1.14
$\text{TiO}_2$	0.37
$\text{Fe}_2\text{O}_3$	3.13
PbO	0.16
SrO	0.10
$\text{ZrO}_2$	0.05
$\text{As}_2\text{O}_3$	0.02
L.O.I	13.86

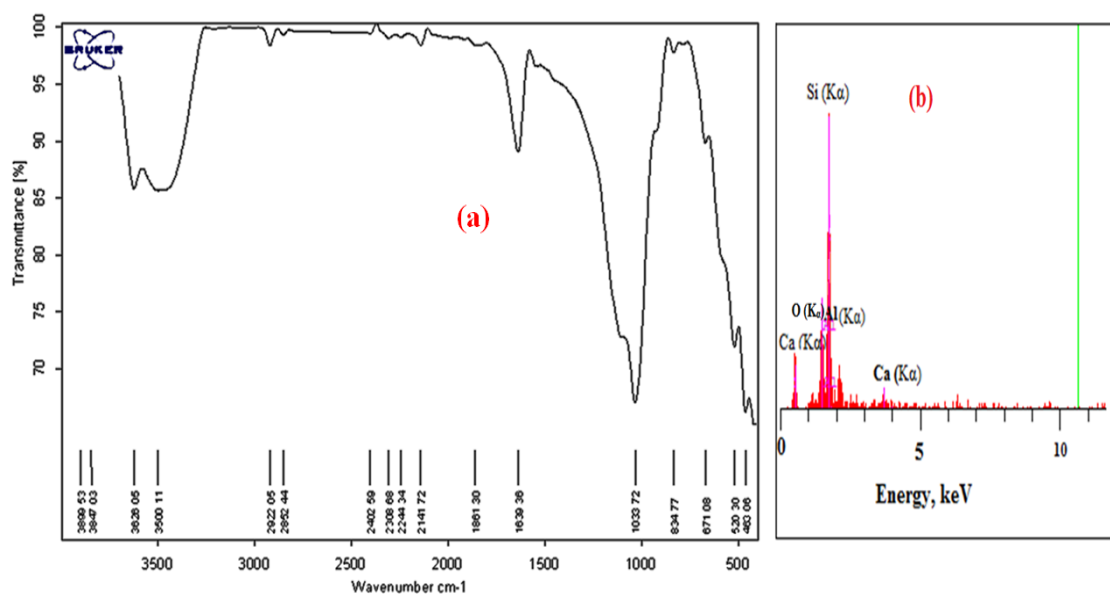


Fig. 3: (a) FT-IR spectrum (b) EDS spectrum of untreated *Ghezeljeh* montmorillonite nanoclay.



### Cation exchange capacity (CEC)

The cation exchange capacity (CEC) is the number of equivalents of exchangeable charge per mass of clay, which is equivalent with the layer charge [52]. The CEC of the *Ghezeljeh* montmorillonite nanoclay was calculated with 0.01 M Cu-triethylentetramine [53,54]. The CEC value of 160.0 meq (100 g)<sup>-1</sup> for the *Ghezeljeh* montmorillonite nanoclay was found, and the very large CEC value approves well with the CEC values for Montmorillonite described in the literature [55].

### Surface area

The specific surface area ( $S_{\text{BET}}$ ), pore volume and pore radius of the *Ghezeljeh* montmorillonite nanoclay were derived from N<sub>2</sub> adsorption isotherms measured at liquid nitrogen temperature (at 77 K) using a Belsorp mini II instrument (BelJapan, Japan). Humidity and vapors on the solid surface or entered in the open pores were rejected by heating under vacuum at 100°C for 12 h prior to the surface area measurements. The *Ghezeljeh* montmorillonite nanoclay owns a specific surface area 90.916 m<sup>2</sup> g<sup>-1</sup>, pore volume of 0.147 cm<sup>3</sup> g<sup>-1</sup> and pore radius of 4.8 nm [42,56].

### Zeta potential measurement

The zeta potential of the *Ghezeljeh* nanoclay was attained from electrophoretic mobility measurements at 21°C, performed using Zetameter apparatus (ZetaCAD instruments) and the measured Zeta potential value is showed in Table 2.

## RESULTS AND DISCUSSION

In order to extraction-preconcentration nickel, lead, and cadmium ions from real samples, standard solutions were subjected to SPE. To optimize the method, the result of adsorbent quantity, eluent characteristics (type, concentration, and volume), pH and type of the buffer solutions, shaking time, sample volume, and initial nickel, lead, and cadmium ions concentration were examined on the adsorption recovery. The effect of desorption time and centrifugation time were also investigated to progress the recovery of method.

### Effect of type and pH of the buffer solutions

To examine the result of pH on adsorption of Ni(II), Cd(II), and Pb(II) ions onto the *Ghezeljeh* montmorillonite nanoclay, pH was changed in the range of 2 to 10 at room temperature by using buffer solutions. The buffer capacity of a buffering agent is at a local maximum when  $\text{pH} = \text{pK}_a$ , and this is where the maximum buffer action can be achieved. The pH variations relatively gradually in the buffer region,  $\text{pH} = \text{pK}_a \pm 1$ , for this reason the suitable range is almost  $\text{pK}_a \pm 1$ . Subsequently, A citrate-citric acid buffer solutions at pH 2-3, acetate buffer solutions at pH 4-6, phosphate buffer solutions at pH 7 and ammonium buffer solutions at pH 8-10 were organized. The consequences are showed in Fig. 4a. Ni(II), Cd(II), and Pb(II) ions were optimally adsorbed on the *Ghezeljeh* montmorillonite nanoclay at pH 5-6. Afterward, in all the experiments, the pH was kept as 5.5 by

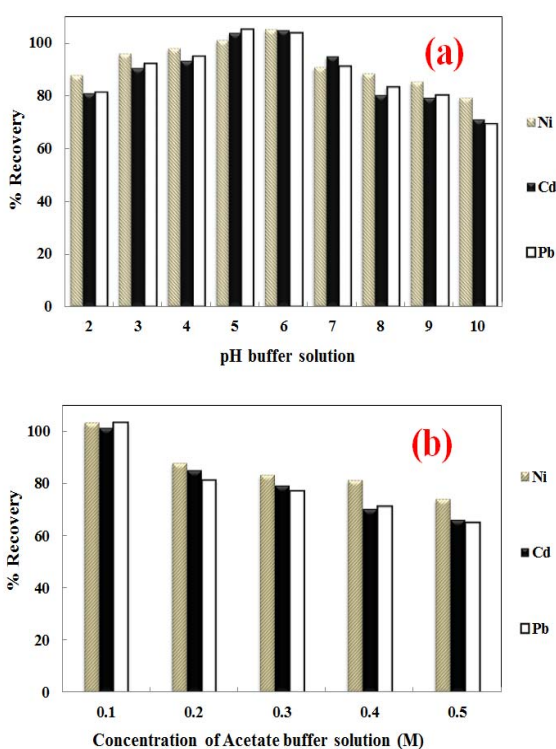


Fig. 4: Effect of (a) pH buffer solution (b) concentration acetate buffer solution on the recoveries of analytes (containing 20 µg of Ni(II), 4.5 µg of Cd(II), and 62.5 µg Pb(II) ions; 25°C; 10 mL 3M HCl (eluent); 0.5 g nanoclay; n=3).

Table 2: The Zeta potential measurement of the *Ghezeljeh* nanoclay

Sample	Dielectric Constant	Electric Field (V cm <sup>-1</sup> )	Mean Mobility (µm s <sup>-1</sup> /V cm <sup>-1</sup> )	Mean Zeta Potential (mV (T=21.31°C))
<i>Ghezeljeh</i> nanoclay	79.810	6.940	-1.880	-25.970 (pH=5.64)

using acetate buffer solution. Clays are recognized to have a negative surface charge in solution, the surface charge changes with changing the pH, and the adsorption of charged species is affected (attractive forces between the positively charged metal ion and the negatively charged clay surface). At low pH values, where there is an 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(II), Cd(II), and Pb(II) ions being precipitated from the solution in the form of hydroxides.

#### Effect of concentration of buffer solution

To examine the effect of concentration acetate buffer solution on adsorption of Ni(II), Cd(II), and Pb(II) ions onto the *Ghezeljeh* montmorillonite nanoclay, concentration of acetate buffer solution in the ranges of 0.1 to 0.5 M at pH 5.5 at room temperature were changed. Fig. 4b displays that the extreme fraction of recovery is gotten at 0.1 M.

#### Effect of amount of adsorbent

Amount of adsorbent is a significant parameter because it determines the capacity of an adsorbent. Eight quantity levels of the *Ghezeljeh* montmorillonite nanoclay were considered: 0.1, 0.2, 0.3, 0.4, 0.5, 1, 1.5, and 2g. The standard solution was 60 mL composing of 50 mL of doubly distilled water containing 20  $\mu\text{g}$  of Ni(II), 4.5  $\mu\text{g}$  of Cd(II), and 62.5  $\mu\text{g}$  Pb(II) ions, and 10 mL of buffer solution added. In order to elute the analytes adsorbed onto the *Ghezeljeh* nanoclay, 10 mL of 3 M HCl solution was used. Analyte contents of the final solution were calculated by flame atomic absorption spectrometry. The adsorption of the metal ions onto the *Ghezeljeh* nanoclay enhanced as the amount of the nanoclay was increased. For subsequent runs of the experiment, 0.5 g of the amount of clay was applied as the optimum of the amount of nanoclay level [3,6,57,58] (Fig. 5a).

#### Effect of eluent characteristics

To attain suitable eluent, HCl and  $HNO_3$  solutions were applied at various concentrations (1-5 M) with varying volumes (5-15 mL) for the elution of Ni(II), Cd(II), and Pb(II) ions adsorbed on to the *Ghezeljeh* nanoclay. The adsorbed ions were readily eluted (desorbed) from the nanoclay only when 10 mL of 3 M HCl solution was used.

#### Effect of shaking time

The influence of shaking time (contact time) for the adsorption of Ni(II), Cd(II), and Pb(II) ions on to the *Ghezeljeh* montmorillonite nanoclay was dignified after 5, 10, 15, 20, and 30 min of shaking by using a mechanical shaker. It was observed that after 5 min, adsorption was completed. Consequently, the metal–clay interactions reached equilibrium in less than 10 min and it was very fast. It showed that, the adsorption positions on the *Ghezeljeh* nanoclay minerals were swiftly covered by the Ni(II), Cd(II), and Pb(II) ions. The contact time of 10 min was further kept in the measurements.

#### Effect of volume of the standard solution

To achieve high preconcentration factor (P.F.), due to the low concentration of Ni(II), Cd(II), and Pb(II) ions in real sample, four quantities of 60, 120, 300, and 600 mL of the feed volumes were investigated. It was found that recovery was over 95% at quantitative up to 300, 300, and 120 mL of sample volumes for Ni(II), Pb(II), and Cd(II) ions,

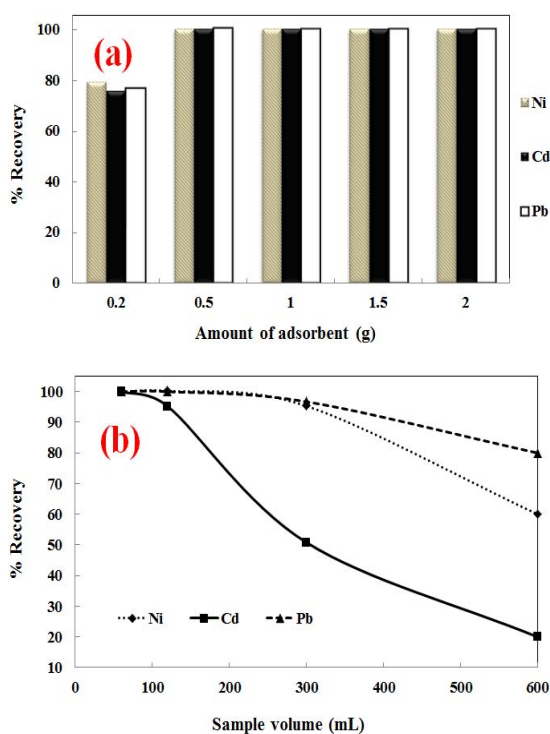


Fig. 5: Effect of (a) amount of *Ghezeljeh* montmorillonite nanoclay (containing 20  $\mu\text{g}$  of Ni(II), 4.5  $\mu\text{g}$  of Cd(II), and 62.5  $\mu\text{g}$  Pb(II) ions; 25°C; 10 mL 3M HCl (eluent); pH 5.5; Acetate buffer solution; n=3), (b) sample volume on the recoveries of analytes (containing 20  $\mu\text{g}$  of Ni(II), 4.5  $\mu\text{g}$  of Cd(II), and 62.5  $\mu\text{g}$  Pb(II) ions; 10 mL 3M HCl (eluent); pH 5.5; Acetate buffer solution; 0.5 g nanoclay, 25°C; n=3).

Respectively. But it declined to below 95% when the feed volumes exceeded 300, 300, and 120 mL. In this study, the final solution volume to be measured by FAAS was 10 mL, therefore the preconcentration factors are of 30, 30, and 12 for Ni(II), Pb(II), and Cd(II) ions, respectively. The consequences are documented in Fig. 5b.

#### Effect of initial metal ions concentration

The adsorption capacity of an adsorbent is defined as the largest extent of metal adsorbed on to 1 g of the adsorbent [3]. In order to find out the adsorption capacity of the *Ghezeljeh* montmorillonite nanoclay, 0.5 g of the nanoclay was added to diverse experiment solutions containing 0.02018, 0.2018, 0.4036, and 0.6054 mg of Ni(II) ions (Fig. 6a); 0.0625, 0.1251, 0.6256, and 1.251 mg of Pb(II) ions (Fig. 6b); 0.0045, 0.020, 0.036, and 0.072 mg of Cd(II) ions (Fig. 6c). The adsorption capacities of the *Ghezeljeh* montmorillonite nanoclay were designed to be 0.806, 0.250, and 0.040 mg g<sup>-1</sup> for Ni(II), Pb(II), and Cd(II) ions, respectively (relative error smaller than  $\pm 5\%$ ). At lower concentrations, a large number adsorption locations on the *Ghezeljeh* montmorillonite nanoclay are available and but it is more problematic to find permitted adsorption locations at high concentrations of metal ions.

#### Desorption time

Desorption time is defined as the length of time an eluent is in contact with the adsorbent having metal ions. The desorption time in this

technique is studied by computing recovery of Ni(II), Pb(II), and Cd(II) ions from the *Ghezeljeh* montmorillonite nanoclay after 5, 10, 15, 20, and 30 min of contact between HCl solution and the nanoclay. Desorption time of 10 min was found to lead to the highest degree of desorption. This value was applied in the remaining tests.

#### Centrifugation time

The influence of centrifugation time on desorption of metal ions from *Ghezeljeh* montmorillonite nanoclay was examined in the time range of 5–30 min with the rotation speed of 3500 rpm. According to these experiments, 30 min centrifugation time is suitable for maximum desorption.

#### Interference from other ions

In order to evaluate the feasible analytical applications of the preconcentration way offered, the effect of numerous foreign ions which interfere with the determination of trace of Ni(II), Cd(II), and Pb(II) ions on *Ghezeljeh* montmorillonite nanoclay in diverse real environmental samples was examined in the optimized conditions. Ions were considered to be interfering when they produced an error larger than  $\pm 5\%$  in the preconcentration and determination of the analyte. The ions frequently present in water do not interfere in the experimental situations applied. Some of the transition metals at milligram per liter levels did not interfere with the recovery of the analytes. These consequences display that the major matrix ions in natural water samples show no

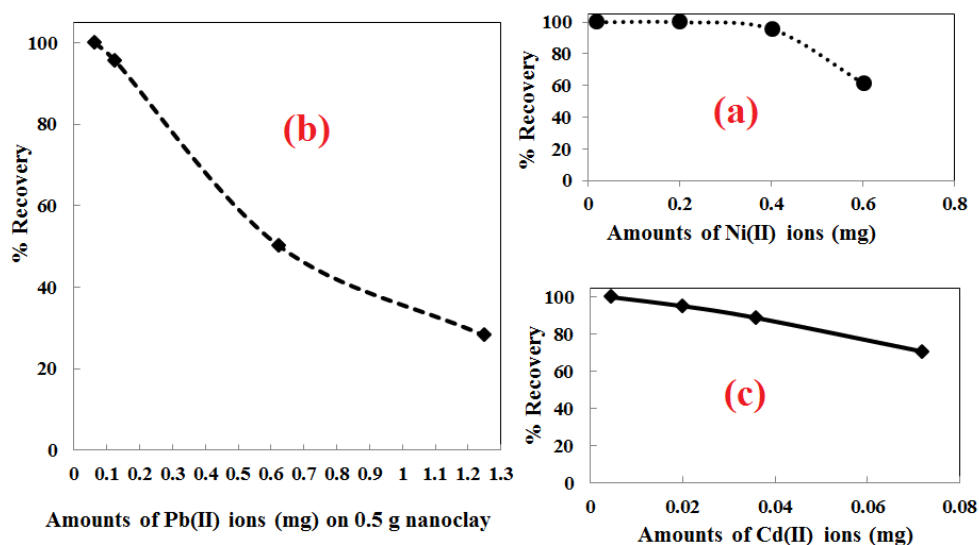


Fig. 6: Effect of initial metal ions concentration (adsorption capacity) on the recoveries of analytes (10 mL 3M HCl (eluent); pH 5.5; Acetate buffer solution; 0.5 g nanoclay; 25°C; n=3).



obvious interference with the preconcentration of Ni(II), Cd(II), and Pb(II) ions (Tables 3-5).

#### Figures of merit

The figures of merit for Ni(II), Pb(II), and Cd(II) ions in the current investigate were calculated under optimal experimental situations after application of the solid phase extraction way to blank solutions. Give attention to, the preconcentration factors were

30, 30, and 12 for Ni(II), Pb(II), and Cd(II) 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  $0.5 \text{ ng mL}^{-1}$  for Ni(II), Pb(II), and Cd(II) ions. The value for the limit of quantification (LOQ) was  $1.6 \text{ ng mL}^{-1}$  for Ni(II), Pb(II), and Cd(II) ions. The dynamic linear range (DLR) for Ni(II) and Pb(II) were from  $1.6 \text{ ng mL}^{-1}$  to  $13.3 \text{ } \mu\text{g mL}^{-1}$ , and for Cd(II) from  $1.6 \text{ ng mL}^{-1}$

Table 3: The effect of additional metal ions on the extraction of  $20 \text{ } \mu\text{g}$  of Ni(II) ion (in optimum conditions;  $n = 3$ )

Ion	Added as	Ion concentration ( $\text{mg L}^{-1}$ )	Salt concentration ( $\text{mg L}^{-1}$ )	Recovery%	RSD%
$\text{Na}^+$	NaCl	630	1600	95	1.9
$\text{Ca}^{2+}$	$\text{CaCl}_2$	36	100	95	3.1
$\text{Mg}^{2+}$	$\text{MgSO}_4$	15	150	95	2.1
$\text{K}^+$	KCl	419	800	95	1.9
$\text{Zn}^{2+}$	$\text{ZnSO}_4$	250	1100	95	2.5
$\text{Fe}^{3+}$	$\text{FeCl}_3$	35	100	95	4.4
$\text{Mn}^{2+}$	$\text{MnSO}_4$	310	950	95	2.5
$\text{Al}^{3+}$	$\text{Al}_2(\text{SO}_4)_3$	55	700	95	3.9
$\text{Cd}^{2+}$	$\text{Cd}(\text{NO}_3)_2$	328	900	95	3.8
$\text{Co}^{2+}$	$\text{Co}(\text{NO}_3)_2$	365	1800	95	4.3
$\text{Pb}^{2+}$	$\text{Pb}(\text{NO}_3)_2$	566	905	95	4.3
$\text{Cr}^{3+}$	$\text{Cr}(\text{NO}_3)_3$	110	850	95	2.6
$\text{Cu}^{2+}$	$\text{Cu}(\text{NO}_3)_2$	215	810	95	2.8

Table 4: The effect of additional metal ions on the extraction of  $4.5 \text{ } \mu\text{g}$  of Cd(II) ion (in optimum conditions;  $n = 3$ )

Ion	Added as	Ion concentration ( $\text{mg L}^{-1}$ )	Salt concentration ( $\text{mg L}^{-1}$ )	Recovery%	RSD%
$\text{Na}^+$	NaCl	670	1700	95	1.6
$\text{Ca}^{2+}$	$\text{CaCl}_2$	29	80	95	4.2
$\text{Mg}^{2+}$	$\text{MgSO}_4$	10	100	95	2.9
$\text{K}^+$	KCl	523	1000	95	2.6
$\text{Zn}^{2+}$	$\text{ZnSO}_4$	228	1000	95	2.1
$\text{Fe}^{3+}$	$\text{FeCl}_3$	76	220	95	4.1
$\text{Mn}^{2+}$	$\text{MnSO}_4$	228	700	95	3.3
$\text{Al}^{3+}$	$\text{Al}_2(\text{SO}_4)_3$	40	500	95	3.9
$\text{Ni}^{2+}$	$\text{NiSO}_4$	163	800	95	2.7
$\text{Co}^{2+}$	$\text{Co}(\text{NO}_3)_2$	375	1850	95	2.2
$\text{Pb}^{2+}$	$\text{Pb}(\text{NO}_3)_2$	87	140	95	2.6
$\text{Cr}^{3+}$	$\text{Cr}(\text{NO}_3)_3$	130	1000	95	3.3
$\text{Cu}^{2+}$	$\text{Cu}(\text{NO}_3)_2$	235	890	95	3.1

Table 5: The effect of additional metal ions on the extraction of  $62.5 \text{ } \mu\text{g}$  Pb(II) ion (in optimum conditions;  $n = 3$ )

Ion	Added as	Ion concentration ( $\text{mg L}^{-1}$ )	Salt concentration ( $\text{mg L}^{-1}$ )	Recovery%	RSD%
$\text{Na}^+$	NaCl	512	1300	95	2.4
$\text{Ca}^{2+}$	$\text{CaCl}_2$	25	68	95	2.9
$\text{Mg}^{2+}$	$\text{MgSO}_4$	21	210	95	3.4
$\text{K}^+$	KCl	728	1200	95	4.2
$\text{Zn}^{2+}$	$\text{ZnSO}_4$	300	1300	95	2.9
$\text{Fe}^{3+}$	$\text{FeCl}_3$	62	180	95	3.8
$\text{Mn}^{2+}$	$\text{MnSO}_4$	319	980	95	4.4
$\text{Al}^{3+}$	$\text{Al}_2(\text{SO}_4)_3$	16	200	95	4.6
$\text{Ni}^{2+}$	$\text{NiSO}_4$	203	1000	95	4.1
$\text{Cd}^{2+}$	$\text{Cd}(\text{NO}_3)_2$	437	1200	95	4.7
$\text{Co}^{2+}$	$\text{Co}(\text{NO}_3)_2$	405	2000	95	3.1
$\text{Cr}^{3+}$	$\text{Cr}(\text{NO}_3)_3$	85	650	95	3.7
$\text{Cu}^{2+}$	$\text{Cu}(\text{NO}_3)_2$	264	1000	95	4.3

ml<sup>-1</sup> to 8.34 µg ml<sup>-1</sup>. The adsorption capacities of the Ghezjeljeh montmorillonite nanoclay were computed to be 0.806, 0.250, and 0.040 mg g<sup>-1</sup> for Ni(II), Pb(II), and Cd(II) ions, respectively.

*Application to real water samples*

The experimental way can be applied for the determination of Ni(II), Pb(II), and Cd(II) ions in real samples with complex media. To validate, the proposed method was used to analyze diverse natural water samples. Before the analysis, the samples were filtered through a Whatman blue band filter paper

and the pH was adjusted to optimum pH level prior than the standard addition. Spiking experiments using multiple standard additions method checked reliabilities; therefore each real water sample was spiked with three standard solutions. Ni(II), Pb(II), and Cd(II) ions level were determined by a Varian 735-ES inductively coupled plasma atomic emission spectrometry (ICP-AES). The recovery was defined as the ratio of the concentration of analytes found to the concentration of analytes spiked. The consequences are recorded in Table 6. The recoveries of the spiked standard solutions were in

Table 6: Extraction of Ni(II), Cd(II), and Pb(II) ions in different water samples (in optimum conditions; n = 3).

Sample	Nickel Added (µg mL <sup>-1</sup> )	Nickel Found (µg mL <sup>-1</sup> )	Recovery (RSD)%	Lead Added (µg mL <sup>-1</sup> )	Lead Found (µg mL <sup>-1</sup> )	Recovery (RSD)%	Cadmium Added (µg mL <sup>-1</sup> )	Cadmium Found (µg mL <sup>-1</sup> )	Recovery (RSD)%
Tap water	-	0.700	-(1.5)	-	1.110	-(1.6)	-	0.020	-(1.4)
	1.009	1.650	94 (1.8)	0.782	1.880	99 (1.8)	0.225	0.248	101 (1.8)
	2.018	2.310	80 (2.1)	1.564	2.500	89 (2.2)	0.450	0.450	96 (1.8)
	3.027	3.060	78 (1.9)	3.128	3.860	88 (2.1)	0.900	0.850	92 (1.9)
Caspian Sea	-	0.200	-(1.7)	-	1.800	-(1.7)	-	0.040	-(2.7)
	1.009	1.150	95 (1.5)	0.782	2.550	96 (2.5)	0.225	0.256	96 (2.5)
	2.018	2.070	93 (1.7)	1.564	3.130	85 (2.7)	0.450	0.445	90 (2.7)
	3.027	2.720	83 (2.6)	3.128	4.450	85 (2.9)	0.900	0.850	90 (2.6)
Karun river (inside city)	-	0.300	-(1.9)	-	1.000	-(3.1)	-	0.050	-(2.1)
	1.009	1.250	94 (2.1)	0.782	1.730	93 (3.1)	0.225	0.250	90 (3.1)
	2.018	2.110	90 (3.3)	1.564	2.370	88 (2.3)	0.450	0.450	88 (3.7)
	3.027	2.90	85 (3.2)	3.128	3.470	79 (3.2)	0.900	0.830	86 (4.2)
Karun river (outside city)	-	0.300	-(2.9)	-	2.100	-(1.9)	-	0.055	-(2.9)
	1.009	1.220	91 (2.8)	0.782	2.800	90 (2.8)	0.225	0.260	91 (3.3)
	2.018	2.120	90 (2.8)	1.564	3.470	88 (2.8)	0.450	0.460	90 (3.7)
	3.027	2.780	82 (2.6)	3.128	4.600	80 (2.6)	0.900	0.820	85 (2.2)
Persian gulf	-	0.200	-(1.8)	-	2.000	-(2.2)	-	0.070	-(1.6)
	1.009	1.080	88 (1.9)	0.782	2.700	90 (2.4)	0.225	0.270	88 (1.9)
	2.018	1.790	79 (1.9)	1.564	3.260	81 (3.8)	0.450	0.440	82 (1.8)
	3.027	2.600	79 (2.2)	3.128	4.450	78 (3.2)	0.900	0.780	78 (1.4)
well water	-	0.400	-(1.7)	-	2.300	-(1.7)	-	0.030	-(1.7)
	1.009	1.381	98 (1.6)	0.782	3.070	99 (1.6)	0.225	0.250	98 (2.6)
	2.018	2.150	87 (1.7)	1.564	3.800	96 (2.7)	0.450	0.460	95 (1.9)
	3.027	2.700	76 (2.8)	3.128	5.000	86 (2.9)	0.900	0.840	90 (2.6)
Haryrood river	-	0.500	-(1.8)	-	2.200	-(1.9)	-	0.05	-(1.9)
	1.009	1.420	91 (1.8)	0.782	2.900	90 (3.8)	0.225	0.260	93 (1.8)
	2.018	2.130	81 (2.1)	1.564	3.450	80 (4.1)	0.450	0.450	88 (3.1)
	3.027	2.900	79 (3.0)	3.128	4.700	80 (4.0)	0.900	0.770	80 (3.0)

Table 7: Comparison between the methods used in this research and similar studies using SPE procedures.

Analytes	Adsorbents	LOD <sup>a</sup>	P.F <sup>b</sup>	Studies
Cd, Cr, Cu, Pb, Zn	rice bran	0.56 - 1.85	100	[58]
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	[59]
Cu, Co, Ni, Fe, Zn, Pb	Gold nanoparticle loaded in activated carbon (Au-NP-AC)	1.5 - 2.8	30	[60]
Fe, Cr(III), Cu, Cd, Pb, Ni	Nanosilicate	0.26 - 0.55	133	[61]
Pb, Fe, Cu	Functionalized activated carbon	0.16 - 0.41	-	[62]
Pb, Cd, Ni, Cu	Gallic acid-modified silica gel	0.58 - 0.92	200	[63]
Pb, Cd, Ni, Cu, Co	Carboxylic acid (COOH) bonded to silica gel	2.1 - 17.5	80, 120	[64]
Ni, Pb, Cd	Ghezjeljeh nanoclay	0.5, 0.5, 0.5	30, 30, 12	This work

<sup>a</sup> LOD: limit of detection (µg L<sup>-1</sup>)

<sup>b</sup> PF: preconcentration factor

the range of 76–101% with low relative standard deviations (less than 5%), which indicates that good recovery can be obtained using the *Ghezeljeh* nanoclay as adsorbent.

#### Comparison between this research and similar studies

The *Ghezeljeh* montmorillonite nanoclay-SPE is compared with the other SPE ways for the extraction-preconcentration of heavy metals in terms of type of analyte, adsorbent, the limit of detection (LOD), and preconcentration factor (PF). As can be realized in Table 7, the *Ghezeljeh* montmorillonite nanoclay shows a relatively low LOD. However, Up to now; Only Soleimani and Hassanzadeh in the Imam Khomeini International University (IKIU) have used *Geleh-Sar-Shoor* for the extraction of metal ions from water, and wastewater [25-28].

#### CONCLUSION

This examination attempted to extraction-preconcentration Ni(II), Pb(II), and Cd(II) ions from diverse real water samples using the *Ghezeljeh* montmorillonite nanoclay as a natural adsorbent. Based on SEM images of *Ghezeljeh* clay, it can be seen that the distance between the plates is nm level. The consequences of XRD, FT-IR and CEC studies of the *Ghezeljeh* nanoclay confirmed that montmorillonite was the dominant mineral phase. The specific surface area of *Ghezeljeh* nanoclay was  $90.916 \text{ m}^2 \text{ g}^{-1}$  whereas the cation exchange capacity was measured as  $160 \text{ meq (100 g)}^{-1}$ . For this purpose, first the adsorbent was readied using the *Galehouse* way and a number of effective parameters on extraction were optimized. The additional metal ions in the aqueous solution already containing Ni(II), Pb(II), and Cd(II) ions frequently do not have a negative effect on the recovery. The limit of detection,  $0.5 \text{ ng mL}^{-1}$ ; limit of quantification,  $1.6 \text{ ng mL}^{-1}$ ; preconcentration factors, 30, 30, and 12 for Ni(II), Pb(II), and Cd(II) ions, respectively; dynamic linear range (DLR) for Ni(II) and Pb(II) were from  $1.6 \text{ ng mL}^{-1}$  to  $13.3 \text{ } \mu\text{g mL}^{-1}$ , and for Cd(II) from  $1.6 \text{ ng mL}^{-1}$  to  $8.34 \text{ } \mu\text{g mL}^{-1}$ ; the adsorption capacities of the *Ghezeljeh* montmorillonite nanoclay were 0.806, 0.250, and  $0.040 \text{ mg g}^{-1}$  for Ni(II), Pb(II), and Cd(II) ions, respectively. The experimental method was used to a variety of real water samples with the recovery being still significant (76-101%). The interaction Ni(II), Pb(II), and Cd(II) ions onto the *Ghezeljeh* montmorillonite nanoclay are quick and

equilibrated in less than 10 min. Therefore, determination of Ni(II), Pb(II), and Cd(II) ions by the *Ghezeljeh* nanoclay is efficient, reproducible, quick and reliable in varied real samples.

#### CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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