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Adsorption of Pb(II) and Hg(II) ions from aqueous single metal solutions by using surfactant-modified ostrich bone waste

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ABSTRACT

In this paper, the application of a stable immobilized cetyltrimethylammonium bromide (cationic surfactant) and laundry detergent (anionic surfactant) on the surface of a biological origin support (ostrich bone waste) was reported as the novel bio-adsorbents for the removal of Pb(II) and Hg(II) ions from aqueous solution. The synthesized bio-materials were characterized by Fourier transform infrared spectroscopy, X-ray diffraction, Brunnauer–Emmett–Teller, SEM-EDX, thermal gravimetric, and point of zero charge. The removal efficiency of the bio-adsorbent was investigated as a function of contact time, pH, initial ion concentration, temperature, adsorbent dosage, and chemical modification process. Equilibrium, kinetics, and thermodynamic studies were also performed for design and evaluate the bio-adsorbents in removing Pb(II) and Hg(II) ions from aqueous solution. The modified ostrich bone with anionic surfactant indicated remarkable capability to remove Pb(II) and Hg(II) ions from aqueous solution. The results showed that the majority of Pb (91.9%) and Hg (87.7%) ions were removed within the first 0–60 min contact with the B-Detergent bio-adsorbent. Langmuir–Freundlich isotherm type model satisfactorily described the Pb(II) and Hg(II) experimental data. The adsorption process was spontaneous and endothermic in nature and followed pseudo-second-order kinetic model.

Keywords: Ostrich bone; Adsorption; CTABr; Laundry detergent

1. Introduction

Due to arid and semi-arid climates of Iran, most of urban, industrial, and agricultural regions are located near the rivers [1]. These activities release the multiple sources of contaminants such as domestic and industrial wastewater, agricultural land drainage, and urban storm runoff [2]. Among these sources, industrial wastes constitute the major source of various kinds of heavy metal (HM) pollution in natural waters [3]. Excessive amounts of HMs in surface and groundwater pose serious public health problems. Therefore, the removal of these ions from water resources is essential in ecotoxicological issues.

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Among the HMs, lead (Pb) and mercury (Hg) due to their toxicity, bioaccumulation, and environmental effects on living organisms, are more appropriate. As a result, the Agency for Toxic Substances and Disease Registry, of the US Department of Health and Human Services, has designated these chemicals as priority pollutants [4]. Pb(II) derived from industrial wastewater discharge of paint pigments, pigments for glazing ceramics, various metal products, petrol additives, and battery manufacturing can produce a wide range of adverse health effects for both adults and children [5]. The permissible limit for Pb(II) in wastewater as set by Environmental Protection Agency (EPA) is 0.05 mg L^{-1} and in drinking water, as set by EU, USEPA, and WHO are 0.010, 0.015, and 0.010 mg L^{-1}, respectively [6]. Mercury that derived from industrial wastewater discharge of chlor-alkali, paper and pulp, oil refinery, paint, pharmaceutical and battery manufacturing causes carcinogenic, mutagenic, teratogenic side effects and also promotes tyrosinemia [7]. The permissible limit for Hg(II) in wastewater and drinking water as set by European Union are 0.005 and 0.001 mg L^{-1}, respectively [8].

Various techniques, including coagulation [9], chemical precipitation [10], electrochemical treatment [11], flotation [12], ion exchange [13], membrane filtration [14], and adsorption [15], have been applied to remove HMs from wastewater and contaminated waters. Recently, biosorption is one of the most effective techniques for HMs removal from wastewaters due to its simplicity, high efficiency, low cost, and applicability for multiple reuses [16].

Animal slaughtering and the food industry provide meat and bone meal, which are by-products, obtained by the removal of fat from animal carcasses by a process of crushing, cooking, and grinding. By-products comprise nearly 60–70% of the slaughtered carcass, of which nearly 40% includes edible and 20% inedible products [17]. These animal by-products can be used as adsorbent for contaminants removal due to naturally, readily available, high adsorption capacity, and low cost [18–23]. From the economical point of view, ostrich bone can be a viable alternative to commercial adsorbents, such as activated carbon or ion exchange resins, for treatment of metal contaminated wastewater [24,25]. The ostrich bone used as naturally and abundantly available adsorbent in this work is an animal by-product produced in large amounts in many parts of Iran. It is also produced in very large quantities in developed and developing countries. Iran is the world's third largest breeder and producer of ostrich meat, after South Africa and China. There are believed to be around 130 Iranian ostrich farms, with local experts insisting that the country possesses the world's best climatic conditions for breeding [26]. Besides setting records, the long-term goal was to create a new cultural appetite for ostrich, which is lower in fat and cholesterol than other meats traditionally popular in Iran.

To our best knowledge, no attention was paid to examining the adsorption capacity of the materials with biological origin, like ostrich bone treated and activated with surfactant group to remove Pb(II) and Hg(II) ions from aqueous solution. Here, we have demonstrated the application of a stable immobilized CTABr (cationic surfactant) and laundry detergent (anionic surfactant) on the surface of ostrich bone host and described the application of the chemically modified bio-adsorbents to remove Pb(II) and Hg(II) ions from aqueous solution. Moreover, equilibrium studies have been performed and the experimental data analyzed using Freundlich, Langmuir, and Langmuir–Freundlich isotherm equations. The adsorption process was assessed by various parameters such as contact time, adsorbent dosage, temperature, pH, and metal solution concentration.

2. Materials and methods

2.1. Materials

All reagents were purchased from Merck or Aldrich and were used without further purification, except that solvents were treated according to standard methods.

2.2. Analytical techniques

The pH of solution was adjusted using 0.1 M HCl/NaOH using a pH meter (Metrohm, 827 pH Lab). The pH at the point of zero charge (pH_{PZC}) of different adsorbents was obtained by the solid addition method [27,28]. The concentrations of Pb(II) and Hg(II) solutions were measured by atomic absorption spectrophotometry using a Perkin-Elmer 3030 instrument. The specific surface area of the different adsorbents was measured using the Brunnauer–Emmett–Teller (BET) method. The pore size was calculated using the Barrett–Joyner–Halenda (BJH) method. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded using a Jasco FT/IR-680 plus spectrophotometer as KBr pellets. X-ray diffraction (XRD) studies were performed using a Philips X'PERT MPD diffractometer for the crystalline structure of the adsorbents. The XRD patterns were recorded in the 2θ range of 10–100°. Scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) analysis were accomplished on a SEM-Seron, model AIS2100, to examine the morphology and composition of the adsorbents. Thermogravimetric analysis (TGA) was performed with a Setaram TG-DTA92, in platinum crucible, under argon atmosphere, from 24 to 800℃ with an increasing temperature rate of 10℃/min. Cation exchange capacity (CEC) of the ostrich bone waste measured by the method was used in the literature [29].

2.3. Preparation of modified ostrich bone

Two surfactants of cetyltrimethylammonium bromide (cationic, CTABr, $C_{16}H_{33}NCH3Br$) and sodium dodecyl benzene sulfonate (anionic, laundry detergent, $CH_3(CH_2)_{11}OSO_3Na$) were used to modify ostrich bones. The modified pristine bone with CTABr and laundry detergent were synthesized by reacting pristine bone with solution containing cationic surfactants, CTABr, and anionic surfactants, laundry detergent. A typical experimental procedure is as follows: 25 g of the pristine bone is dispensed in 0.5 L of distilled water. Then a certain amount of either CTABr or detergent (the equivalent of 100% CEC of surfactant) is added and the suspension is subjected to mechanical stirring for 1 h on heater at 70℃. However, in measuring the CEC of pristine ostrich bone by the method of NH4Cl–NH4OAc [29], pristine ostrich bone CEC is found to be 59.86 cmol kg^{-1} mineral. The final material is separated by centrifugation and washes with 50% (v/v) of water and ethanol mixture. The resulted sample is dried at 60℃ overnight, and mechanically ground with a mortar and then passes through 100-mesh sieve.

2.4. Adsorption measurements

Different metals ion concentrations (from 5 to 100 mg L^{-1}) were freshly prepared in a solution of deionized water. Sorption experiments were carried out in batch conditions: 0.1 g of modified bone sample was shaken with a 30 mL of the inorganic pollutant, at a controlled temperature of 25℃. The time required to work in equilibrium condition was determined by preliminary kinetic measurements. The kinetic tests of all HMs showed no significant variation in sorption after 24 h. After centrifugation at 3,000 rpm for 5 min, the liquid phase was separated and the solute concentration was determined by atomic absorption spectrophotometer. The amount adsorbed was calculated from the formula:

$$q_e = V \cdot (C_0 - C_e)/m \tag{1}$$

where C_0 and C_e are the initial and equilibrium liquid-phase concentrations (mg L^{-1}) of adsorbates; V is the volume of the solution (L); and m is the amount of adsorbent (g). In this method, it is assumed that the change in volume of the bulk liquid phase is negligible because the solute concentration is small and the volume occupied by the adsorbent is also small. The amount of HMs adsorbed on the sample was calculated based on a previously determined calibration curve. And it acts not only as a source of adsorption centers, but also enables the ion-exchange process.

3. Results and discussion

3.1. Effect of procedure of pretreatment on Pb(II) and Hg(II) ions adsorption

Preliminary experiments showed that the pristine ostrich bone has the low capacity to adsorb Pb(II) and Hg(II) ions from the wastewater. Pristine ostrich bone contains more than 80% organic compounds which could block the inorganic phase and suitable active sites of the bone (i.e. hydroxyapatite is known to bind metals strongly [18–24,30], which were shown earlier to promote heavy-metal-ion adsorption through preferential ion exchange [24,31,32]). So in this work various processes of pretreatment are designed to ostrich bone with the aim of enhancing the metal adsorption capacity by opening up the physical structure and framework to give more active sites and/or by obtaining suitable chemical modification of the available functional groups.

Laundry detergent is believed to clean some soluble organic compounds from the pristine bone without suffering the nature and amount of metal binding sites already present in the pristine bone, therefore opening up the pores and framework of the pristine bone and increasing the number of available binding sites such as sulfonate groups, as consequence of the immobilization of some anionic surfactant through their hydrophobic chains on the pristine bone [33]. CTABr modification will have the strong effect of removing the fat tissues and organic compounds and either changing the characteristic of adsorbent [33]. The structures of the bone samples were confirmed by SEM, EDX, BET, thermal gravimetric (TG), FT-IR, and XRD.

3.2. SEM analysis

SEM has been a primary tool for studying the changes of surface morphology, distribution, and fundamental physical properties of the adsorbent before and after the chemical modification. Fig. 1

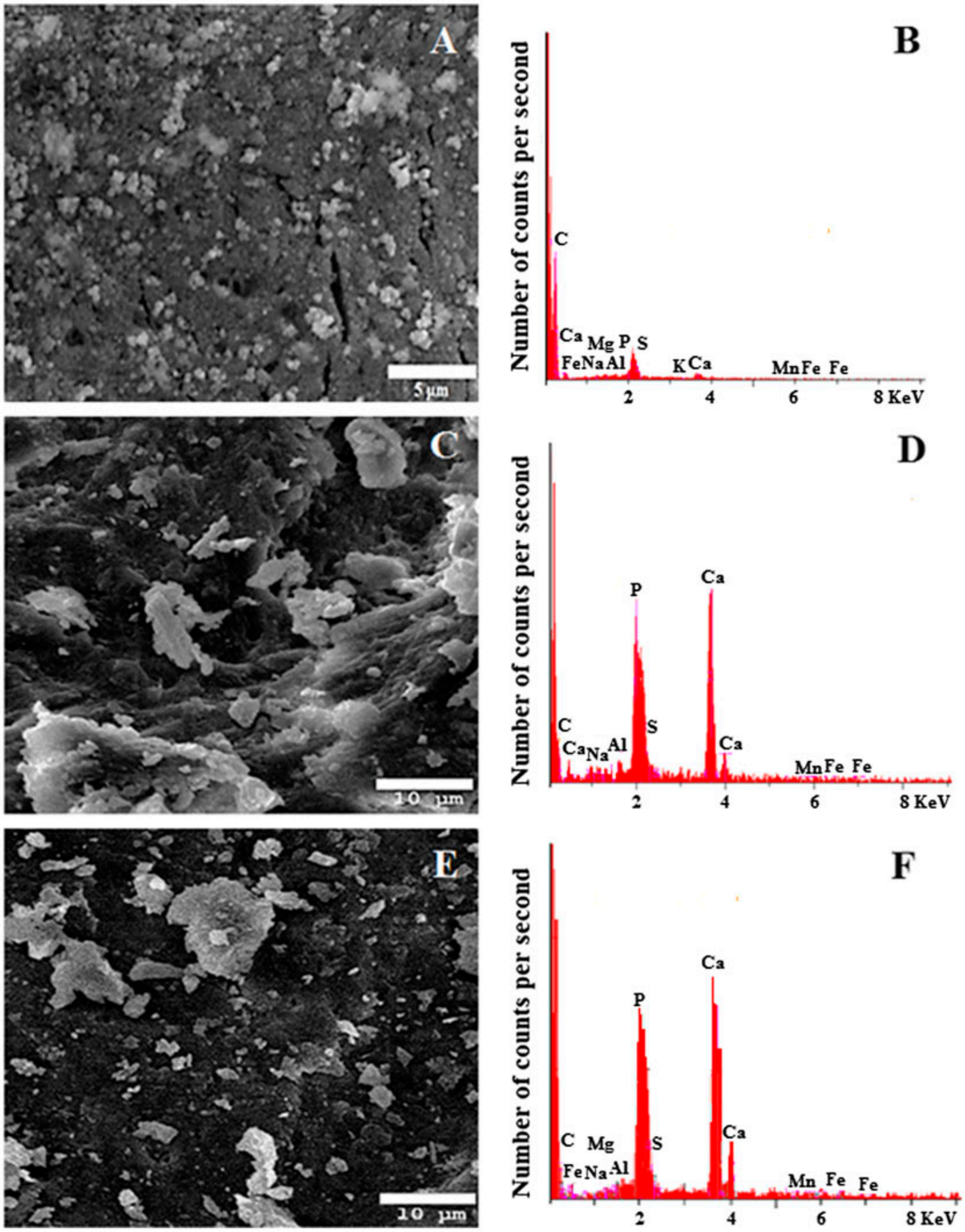

Fig. 1. SEM-EDS analysis of (A and B) Pristine ostrich bone; (C and D) B-Detergent; (E and F) B-CTABr.

shows the morphology of ostrich bone, B-CTABr, and B-Detergent. It is clear that ostrich bone has an assemblage of fine particles of irregular shape and size with plenty of small ravines. B-CTABr and B-Detergent shows an uneven and folded surface morphology which could be due to removing of organic compounds by cationic and anionic surfactant treatment and increasing the inorganic phase (a heterogeneous surface area and porous internal structure were observed). However, before the modification of ostrich bone, (Fig. 1(A)), pristine bone pores were not visible. This shows that the modification with surfactant has uncovered the entire external bone surface from fat tissues and organic compounds while a surfactant thin layer may be covered on the modified bone samples. Therefore, B-CTABr and B-Detergent micrographs show a flexible and porous surface, which could be useful for the contaminations removal.

3.3. EDX and BET analysis

The chemical compositions of the pristine and modified ostrich bone after CTABr and laundry detergent treatment were determined by EDX. The ostrich bone contains relevant amounts of animal nutrients like C, Ca, P, K, and Mg (Fig. 1(B)). In addition, the bone contains a number of elements that are vital to animal in small doses, that is, micronutrients, but also generally contain small amounts of undesirable HMs. EDX analysis of ostrich bone from an average of scanned points shows the strong C signal originates from the fat tissues and organic compounds adhesive the framework of pristine bone. CTABr and laundry detergent treatment remove fat tissues as a change in the color of the extraction liquid can also be visualized, because the extraction liquid is dirty brown. During the modification reactions, the carbon content of pristine bone after CTABr and laundry detergent modification decreased from 83.0 to 34.6 and lower than 31.7 wt.%, and the calcium and phosphor contents increased. Also, the laundry detergent treatment may induce negative charge by immobilization of anionic surfactant from its hydrophobic chains, which increases the active sites of the modified bone (the sulfur and sodium contents of B-Detergent after modification increased) (Fig. 1(D)). Anionic surfactant of detergents is similar to the cationic ones, with a hydrophobic component; but, instead of the cationic quaternary ammonium group, the anionic surfactants have sulfonate group. The sulfonate center is negatively charged. In the laundry detergent treatment process, it is believed that anionic surfactant immobilized through its carbon chains to form monolayer on the ostrich bone to add sulfonate active sites (Fig. 2). So, the force and interaction balance for the surfactant monolayer sorption through the hydrophobic chains of anionic surfactant is the summation of (I) the electrostatic repulsion between the negatively charged pristine bone surface and the negatively charged head groups (sulfonate group as the polar end); (II) the tail–tail hydrophobic interaction between the covered fat tissues and organic compounds of the pores and surface of the pristine bone and the hydropholic chains of surfactant, which is of the London van der Waals type; (III) the electrostatic repulsion between the positively charged counterions of pristine bone (Na$^+$, K$^+$, Ca^{2+}, and Mg^{2+}) and surfactant (Na$^+$) in solution; and (IV) the electrostatic repulsion between the head groups of the first layer and the second layer. In fact, the immobilized detergent readily react with wastewater contaminations (Pb(II) and Hg(II) ions) to give the heterogeneous HMs [33]. However, it is believed that cationic surfactant (CTABr) immobilized through its end polar heads on the ostrich bone to decorate the surface of the ostrich bone with alkyl chains groups (Fig. 3). Furthermore, the EDX results represent that non bromine was detected on the surface of B-CTABr, thus, CTABr molecules is most probably immobilized on the ostrich bone surface through a mode of monolayer (Fig. 1(F)) [34–36].

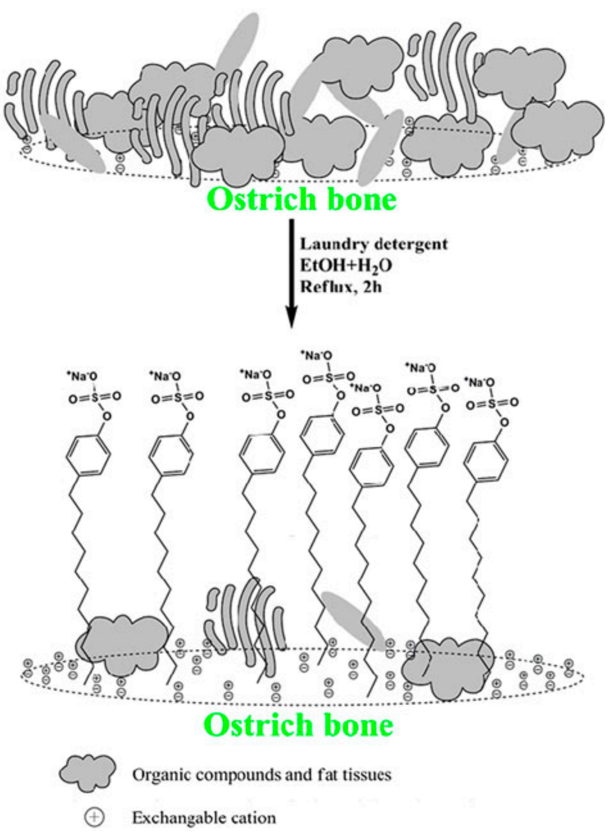

Fig. 2. The proposal chemical structure for the immobilization of anionic surfactant on B-Detergent.

The textural properties of the samples, evaluated from the nitrogen adsorption at $-196\,^{\circ}$C revealed that the specific surface area (SBET) and either the average pore size of B-Detergent and B-CTABr, increased than the pristine bone, which again demonstrated the removing of organic compounds from the pores of the ostrich bone after chemical modification (Table 1). However, the greater specific surface area and average pore size of B-Detergent give an increase in the approachability of active sites of the adsorbent in

Table 1
The physicochemical properties of the materials

	Ostrich bone	B-Detergent	B-CTABr
Total surface area ($m^2\ g^{-1}$)	3.69	7.29	4.18
Average pore size[a] (Å)	43.22	51.18	45.02

[a]The pore size calculated using the BJH method.

contact with contaminated water, which lead to a better efficiency of the modified bone in removing of HM ions.

3.4. IR spectroscopy

Inspection of infrared wave numbers (cm^{-1}) of significant valence vibrations of the pristine bone powder before modification, after modification with CTABr and laundry detergent show striking changes promising with chemical modification, which are collected in Fig. 4. The bands at 1,625–1,665 cm^{-1} are related to organic tissue and water of pristine ostrich bone, while the $–CO_3^{-2}$ band intensities of unmodified bone appear at 1,413 and 872 cm^{-1} [37,38]. However, the pristine bone shows the characteristic absorption bands of symmetric and asymmetric stretching vibration of the CH_2 and CH_3 at around 2,922 cm^{-1}, 2,852 cm^{-1}, and 1,470–1,455 cm^{-1}, while the presence of a definite band at 1,744 cm^{-1} is due to carbonyl groups (–C=O). The spectrum in the C–H stretching region shows absorption maxima at 3,065 cm^{-1}, which is typical of the C–H stretching vibration of the aromatic ring.

As can be seen from the Fig. 4(A), the characteristic vibration bands of O–P–O bonds of calcium phosphate appeared in all the samples as follows: 1,165 cm^{-1} ($HPO_{4\text{-}2}$ group, P–O–H in-plane and out-of-plane deformation modes), 1,028 and 1,100 cm^{-1} (v_3, P–O asymmetric stretching vibrations), 960 cm^{-1} ($v_1$sym, P–O stretch), 603 cm^{-1} (v_4, P–O stretch), −560 cm^{-1} (v_4, P–O stretch and P–O bending) [37,38]. FT-IR also bestows an indication of the inorganic phase of the bone (mineral crystallinity of hydroxyapatite). In fact, two bands in the regions 1,028–1,100 cm^{-1} attribute to hydroxyapatite while amorphous calcium phosphate appears a broad single band. However, the characteristic vibration bands of hydroxyapatite are hardly obvious in unmodified bone which could be due to the high content of organic phase (collagen, fat, and organic tissue) which disguises the features of the mineral phase and decreases the crystallinity of hydroxyapatite. Furthermore, infrared wave numbers of bone powder comprise some characteristic absorption bands related mainly to the peptide bonds (–CONH–) which known as amide I, amide II, and amide III. The weak intensity of the vibration bands in the range of 1,700–1,600 cm^{-1}, attribute to C=O stretching vibrations of the amide I and are assigned as a useful indicator of different types of protein secondary structure [39]. Indeed, the α-helical and the -sheet structure of the protein giving a maximum near 1,655 cm^{-1} and 1,630 cm^{-1}, respectively. The amide I peak of unmodified bone appeared at 1,641 cm^{-1} and 1,646 cm^{-1}. The amide II peaks which appeared in the region of 1,520–1,540 cm^{-1} are assigned to N–H and C–H bending and stretching vibration. The amide III band which falls in the range of 1,220–1,300 cm^{-1}, is attributed to the phase combination of C–N stretching, N–H in plane bending, and some contribution from C–C stretching and C=O bending vibrations. Natural proteins and peptides contain a disulfide bond (–S–S–), which appears as stretching vibrations near 510, 525, and 540 cm^{-1} [40,41]. Therefore, the main band at 507 cm^{-1} and the ones at 521 and 530 cm^{-1} with lower intensities were attributed to the disulfide bond of pristine bone (Fig. 4(A)).

The band intensities of 1,656, 1,538, 1,465 (bending vibration of $–CH_3$), 1,417 (the symmetric deformation CH_2 vibrations for the immobilized CTABr [42,43]), 1,352 (N–C bending), 1,030 (vibration bands of hydroxyapatite), 603 cm^{-1} (v_4, P–O stretch), 560 cm^{-1} (v_4, P–O stretch and P–O bending), and the main ammonium ions (NR^{4+}) bond at around 3,270 cm^{-1} increased with modification of bone with CTA^+Br^- (Fig. 4(B)). The absorption at 3,270 cm^{-1} was attributed to water adsorbed on the structure of the bone [44]. It can be seen from the spectra that this band weakened with the treatment of ostrich bone with CTABr. Therefore, this phenomenon is a good indication of the alternation of the property of pristine bone from hydrophilic to hydrophobic (the electrostatic attraction between the negatively charged ostrich bone surfaces and the positively charged head groups of CTABr, result in the sorbed most of the surfactant cations monolayer with alkyl chains orienting toward the solution) (Fig. 3).

To prove the proposed mechanism in Fig. 2, the immobilization of laundry detergent on the pristine bone was studied by FTIR (Fig. 4(C)). The band intensities of 2,922, 2,852, 1,744, 1,470–1,455 related to the organic tissue decreased with modification of bone with laundry detergent. The broad band from 2,450 to 3,400 cm^{-1} for B-Detergent attributes to stretching modes of hydrogen bonded of adsorbed H_2O molecules which demonstrates increasing hydrophilicity of modified bone with detergent rather the unmodified one (the molecules of H_2O are more adsorbed over B-Detergent than to the one modified with CTABr). Indeed, the anion-active molecules are usually thought to be adsorbed on the fiber surface through their lipophilic chains so that the polar heads are outwards [45]. Therefore, the detergent is believed to adsorb chiefly on the surface of the pristine bone through the organic chains monolayer so their polar heads are outwards which causes increasing hydrophilicity of modified bone with detergent. The modification of the bone powder with detergent was an efficient procedure in reducing the amount of organic phase and destroys the organics that cover the framework of bone, increasing inorganic phase (increasing the band intensities of 1,030, 603, and 560 cm^{-1}) and consequently raising the accessible amount of the active sites of the bone (the fat tissue seems to be replaced with surfactant in the modified bones as compared to pristine bone).

As a consequence, the appearance and disappearance of different peaks show that the chemical modification of ostrich bone with cationic and anionic surfactant successfully induced different and distinctive properties onto the structure of bone as shown in Figs. 2 and 3.

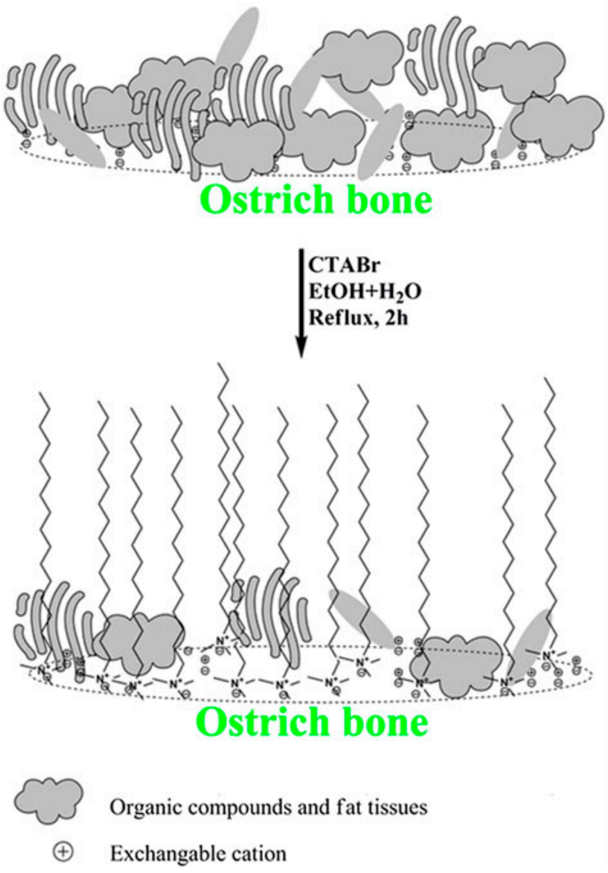

Fig. 3. The proposal chemical structure for the immobilization of CTABr on B-CTABr.

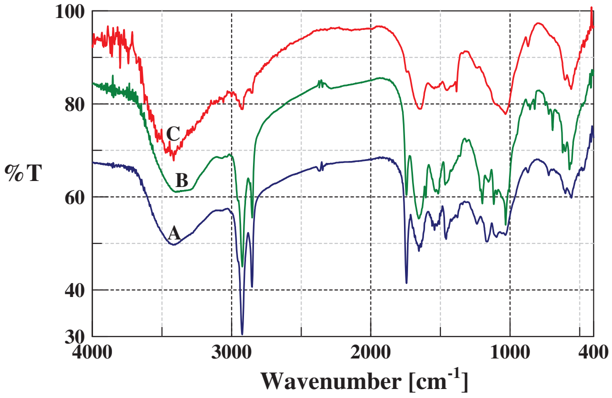

Fig. 4. FT-IR spectra of the ostrich bone (A); B-CTABr (B); B-Detergent (C).

3.5. Thermal gravimetric analysis

Thermal stability of the pristine bone and B-Detergent was studied with TGA in Ar atmospheres, which heated from the room temperature to 800℃ with a ramping rate of 10℃/min (Fig. 5). Thermal analysis (TG) of bone showed third stages of weight loss, stage I (81.9–231℃) corresponds to the desorption of physically held water (3.3 wt.%), mainly the attracted and loosely bound water remove from inward framework and surface of bone, and Stage II (231–494.5℃), proving a process of fast degradation and burning of organic components (bone marrow, fat tissue, and collagen are pyrolyzed to water and carbon dioxide) as well as the release of some strongly bounded crystal water [46]. At the third stage (494–800℃), weight loss decreased with lower rate than the stage II and the weight loss was very slow above 625℃ (14.0 wt.%). The additional weight losses in stage III could be explained due to the several phenomena; burning of the residual organic components, the oxidation of carbonated from the framework of bone to carbon dioxide and releasing of the possible lattice water [46]. However, B-Detergent showed

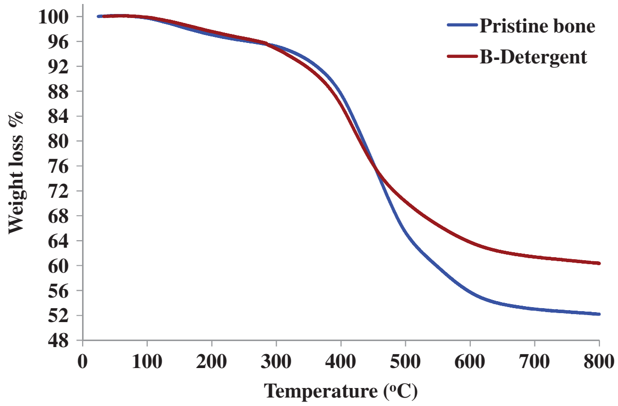

Fig. 5. TGA of bone samples.

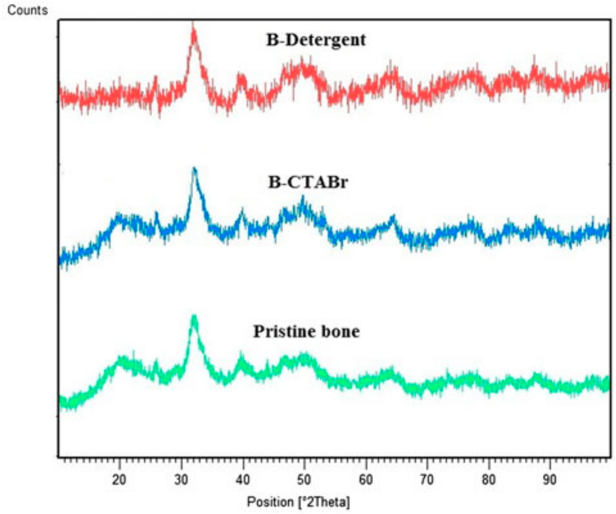

Fig. 6. Wide-range XRD of the unmodified and modified ostrich bone with CTABr and laundry detergent.

third distinct steps: at 83.1–276.8, 276.8–450.5, and 450.5–800°C (Fig. 3). Stages I and II (81.1–450.5°C) are due to desorption of water molecules from the framework of B-Detergent and either evaporation and decomposition of the immobilized detergent. Observation from TG curves reveals that B-Detergent had lower mass loss than pristine bone below 270°C, which is an indicative of more free water molecules strongly adsorbed into the structure of modified bone. This could be explained that the adsorbed anionic surfactants increased the surface energy of the bone, and converted the hydrophobic bone surface to the hydrophilic one [46], which are in agreement with the FTIR results.

The additional weight losses in stage III may be explained due to the calcination of coke and decomposition of the remained organic and carbonic compounds. As a result, from the comparison of thermogram analysis of samples, it is concluded that the weight losses of the modified bone at stages II and III significantly decreased and, in fact, thermal stability and mineral content of modified bone with detergent improved (mineral content, 60.5 wt.%) rather than unmodified one (mineral content, 52.4 wt.%).

3.6. X-ray diffraction

The XRD patterns of pristine and modified ostrich bone are given in Fig. 6. Comparison of XRD pattern to JCPDS file confirms the presence of a major calcium hydroxyapatite (CaHAP) phase [$Ca_{10}(PO_4)_6(OH)_2$], while the broad and intense background were attributed to the collagen, fat tissues, and other organic compounds [44,46]. These results clearly show the poor crystallinity of pristine ostrich bone even after chemical modification, but the XRD patterns of the modified samples show that calcium phosphate peaks become somewhat higher in intensity after treatment by CTABr and Detergent which is due to the removal of inward organic compounds from the framework of ostrich bone and increasing the mineral phase. An increase in the inorganic phase fraction of modified bone sample was also appeared and characterized by an increase in the region intensity at 2θ in 26°, 32°, and 40–50° θ for B-CTABr and B-Detergent, respectively. The peaks intensity of B-Detergent is higher than B-CTABr (peaks at 32, 39, 50, 52, and 64) which further demonstrated the ability of detergent in removing of organic tissues from the framework of the pristine bone (B-Detergent has higher surface area (7.29 $m^2 g^{-1}$) than B-CTABr (4.18 $m^2 g^{-1}$)) by interaction of anionic surfactant through van der Waals force between hydrocarbon chains and organic compound of the pristine bone. However, the chemical modification did not create remarkable alters of HAP original crystallinity [47].

To understand the mechanism of this research, the XRD patterns of the reaction product of aqueous Pb(II) and Hg(II) with B-Detergent are presented in Fig. 7. XRD analysis showed that the weak peaks (a new phase) at the left shoulder of the big peaks of HA (the peaks at 30.1–30.2 (2θ)), which matches closely to M- (Pb(II) and Hg(II)) hydroxylapatite ($M_{(10\text{-}x)}Ca_x(PO_4)_6(OH)_2$; pyromorphites are the thermodynamically most stable M-bearing minerals [22]) appeared after B-Detergent was incubated in Pb(II) and Hg(II) solution for 3 h (Fig. 7). In agreement with XRD analysis results, we demonstrated that the sorption process of Pb(II) and Hg(II) caused the increasing of the final pH values in the range from

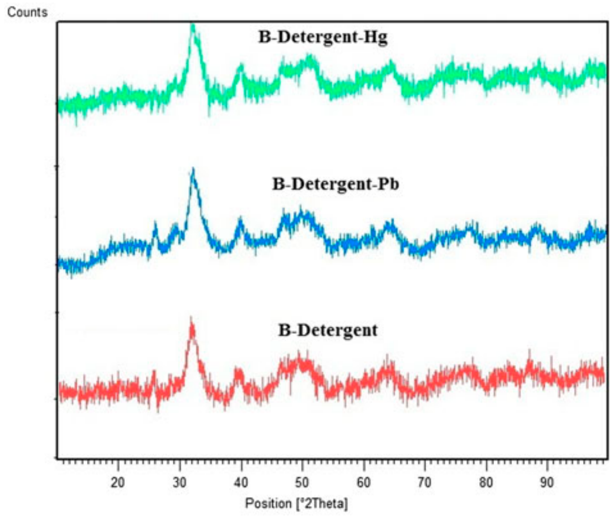

Fig. 7. XRD patterns of B-detergent before and after incubation with Pb(II) and Hg(II) ions solution.

4.1 to 7.5 (Fig. 8). The increase in equilibrium pH suggests that Ca^{2+} ions and the Na^+ ions from the sodium sulfonate groups of loaded detergent are released from the bone structure into the aqueous phase.

The presence of some XRD-detectable Pb- and Hg-minerals suggested that the mechanism of adsorption of Pb and Hg ions on the framework of modified bone predominantly performed by their diffusion into HA and the liberation of cations (Ca^{+2}) originally comprised within HA, the Na^+ ions from the sodium sulfonate groups of loaded detergent (ion–ion exchange mechanism) and a mechanism involving HA dissolution followed by metal insoluble salts precipitation [46]. However, some of the Pb(II) and Hg(II) ions may be adsorbed by the interactions of Pb and Hg with the lone pair of electrons associated with the negatively charged of functional groups chemisorbed (including anionic surfactant, remaining amino acids and phosphate; $–SO_3Na$, –ONa, –COONa, –NH, and –P–OH) via electrostatic interactions and coordination to the inner vacant d-orbitals of the Pb(II) and Hg(II) ions to form a coordination bond, which reduce the role of Pb (II) and Hg(II) ions in pyromorphite formation.

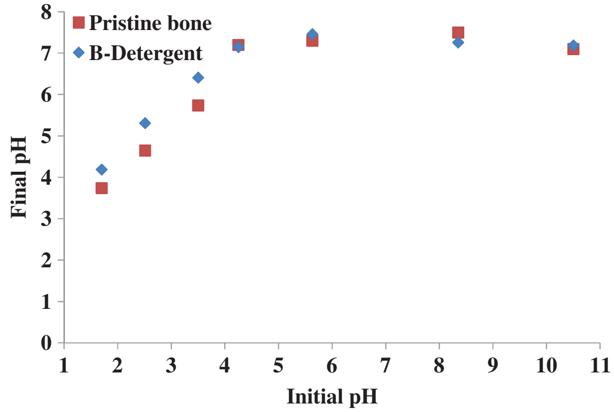

Fig. 8. The effect of initial pH on final pH values.

3.7. Adsorption studies

3.7.1. Effect of initial pH on metal ion adsorption and the zeta potential

The effect of pH plays an important role on the active sites of bio-adsorbents as well as the metal speciation during the adsorption reaction [48]. To evaluate the influence of pH on the adsorption capacity of the bone samples, experiments were performed at initial concentration of 2 and 10.0 mg L^{-1}, and pH range 1.5–11 (Fig. 9).

As shown in Fig. 9, the modified bone indicates higher Pb(II) and Hg(II) ions sorption capacity than pristine bone in different ranges of pH. The lowest Pb (II) and Hg(II) sorption capacity of B-Detergent (64 and 26%, respectively) were found at an initial solution pH of 1.5. On the other hand, as the initial pH increased to 5.5 and 6.5 for Pb(II) and Hg(II) ions, respectively, sorption capacity increased to more than 85 and 95% for Pb(II) and Hg(II) ions and decreased in the initial pH range above 6.5 for Hg(II) ions (>95%). However, the decrease in Hg(II) removal may be due to the formation of soluble hydroxylated compound ($Hg(OH)_2$) [7,8]. The effect of Hg(II)

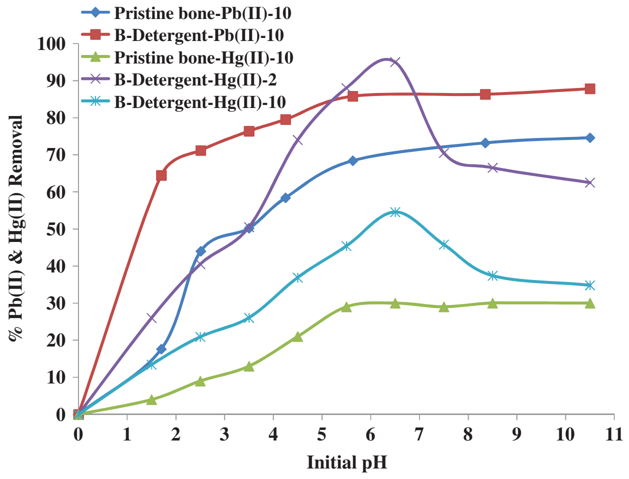

Fig. 9. Effect of pH on Pb(II) and Hg(II) ions sorption from aqueous solution.

concentration on the efficiency of adsorbent was also studied. As the Hg(II) ions amount increases in solution, the removal efficiency decreases at constant pH. This phenomenon may be explained by the following reasons: at low Hg(II)/B-Detergent ratio, the Hg(II) ions adsorption performs on the high-energy sites, but with increasing the Hg(II)/B-Detergent ratio the higher energy sites are saturated and adsorption commences on the lower energy sites, concluding in a decrease in adsorption efficiency. Thus, the pH curves are shifted to alkaline pH, the similar results have been previously published in the literature [8,20,24,33].

The observed lower uptake in an acidic medium may be attributed to the partial protonation of the active sites (the dominant active sites of B-Detergent are $–SO_3H$, –P–OH, and ≡Ca–O–H species) and the competition of H^+ with metal ions. Based on the results of previous published data, the most of lead and mercury species in the solution at acidic pH (1.5–7.0) are Pb(II), $Pb(OH)^+$, $Pb(OH)_2$, Hg(II), and $Hg(OH)^+$ [7,49]. For adsorption sites on the pristine and modified bone (the active sites are closely associated with hydronium ions H_3O^+, that is, restricted the approach of Pb(II) and Hg(II) ions, as a result of the repulsive force), fewer groups are available for metal ions to bind with [46].

In order to a better comprehend of the net charge of the adsorbent surface at the different pH solution, the point of zero charge (pH$_{ZPC}$) of the bone samples were measured. The results of pH$_{ZPC}$ determination are shown in Fig. 10. The pH$_{ZPC}$, ZPC is defined as the pH at which the total surface charges become zero, of all bone samples showed the same behavior. The modified samples indicate a lower pH$_{ZPC}$ (pH$_{ZPC}$ of the B-Detergent was estimated to be about 6.12, with increasing amount of sulfur enrichment; SO_3^- groups) in comparison with unmodified bone (pH$_{ZPC}$ 7.8), which confirm that the surface of the B-Detergent has been modified after chemical modification in presence of laundry detergent.

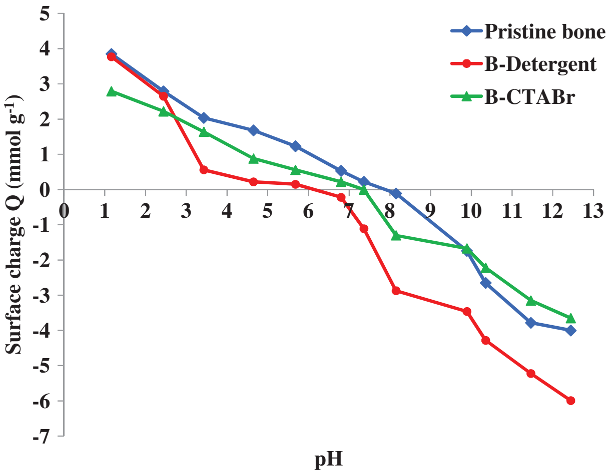

Fig. 10. Zeta potential of ostrich bone, B-CTABr and B-Detergent as a function of pH.
Notes: CBone samples = 2.5 g L^{-1} and 10–3 mol L^{-1} solution of KNO3). Experimental error: ±4 mV.

To go a little further into the adsorption reaction mechanism proof, and in order to evaluate the effect of adsorbents addition (pristine bone and B-Detergent) to the Pb(II) solution initial pH (pH$_i$), pH alternation of solution was studied after 3 h. In the pH range of below 5.0, equilibrium pH (pH$_f$) was increased, which could be due to the inducing of calcium release (ion exchange mechanism) from the bone framework to the solution (Fig. 8) [50]. The amount of Ca(II) released from B-Detergent is higher than Pristine bone (data not presented), which may be attributed to removing of B-Detergent organic compounds and their partial removal from the pores of the inorganic framework of bone (see results of BET and average pore size), to increase the accessibility of adsorbent active sites and also accelerate the releasing of Ca(II) from inorganic phase easily.

Furthermore, the appearance of peaks belonging to pyromorphite (Fig. 7) on B-Detergent XRD analysis verifies the production of $M_xCa_{(10-x)}(PO4)_6(OH)_2$ (M = Pb and Hg) and also the dissolution/precipitation mechanism (Calcium atoms have been substituted by HMs) [49,50]. However, in the range of the lower initial pH values (pH < pH$_{ZPC}$) consumption of protons from the solution by the protonation of bone active sites ($–SO_3^-$, $–P–O^-$, and $≡CaOH^0$ groups) results in a pH$_f$ increase. On the other hand, the pH$_f$ decrease takes place in the range of higher pH$_i$ (above pH 8.0) that may be due to OH^- consumption via deprotonation of $–SO_3H$, –P–OH, and $≡Ca–O–H^{2+}$ active site (Fig. 6). Therefore, the $≡Ca–O–H^0$ groups and negatively charged active sites of the adsorbent ($–SO_3^-$ and $–P–O^-$ species) predominate in alkaline solutions, causing the structure of modified bone (B-Detergent) become more negatively charged than pristine bone in alkaline solutions (pH$_{ZPC}$ of B-Detergent is lower than the unmodified bone), so the electrostatic attraction of B-Detergent to Pb(II) and Hg(II) ions increased with increasing pH than the unmodified bone, Fig. 2 (the HM ions sorption by immobilized anionic surfactant functional groups) [22].

3.7.2. *Effect of the initial concentration on the uptake*

The results of the experiments with varying initial Pb(II) and Hg(II) ions concentrations (0.5–30 mg L^{-1})

over the bone samples are illustrated in Figs. 11 and 12. When the initial Pb(II) and Hg(II) ions concentration were increased, the removal efficiencies of metal ions by B-Detergent reached to 73 and 47%, respectively, at 25˚C for 24 h. The increase in the loading capacities of sorbents with increasing Pb(II) and Hg(II) concentrations is due to the interaction between metal ions and adsorbents which provides the vital driving force to defeat the resistances to the mass transfer of metal ions between the aqueous and the bone samples [24]. However, the removal of HMs in this study was in the order of Hg(II) < Pb(II), with the same trend of hydrated radius as Hg(II) (0.234 nm) < Pb(II) (0.254 nm) [51]. The order of adsorption found for Pb (II) and Hg(II) ions on the bone samples was: B-Detergent > Pristine bone > B-CTABr. The Pb(II) and Hg(II) ions removal increased dramatically and the adsorption equilibrium was achieved much faster with the chemical modification of ostrich bone with anionic surfactant and decreased with cationic surfactant (CTABr). It is in agreement with the proposed mechanism of monolayer immobilization of CTABr through its head polar groups with alkyl chains orienting toward the solution, which could change the property of ostrich bone from hydrophilic to hydrophobic and either decreasing accessibility of the adsorbent active sites (Fig. 3).

The strong affinity of the modified bone sample (B-Detergent) for the metal ions arises from the removal of organic compounds from the framework of pristine bone and also adsorbed monolayer Detergent from its carbon chains with head polar groups (sulfonate active sites) orienting toward the solution (dissimilar the immobilization process of CTABr on ostrich bone), which could change the property of ostrich bone from hydrophobic to hydrophilic and either increasing accessibility of the adsorbent active sites.

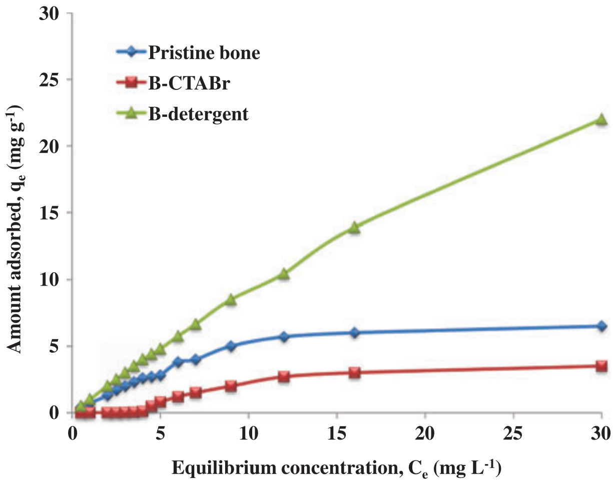

Fig. 11. The effect of initial concentrations for the adsorption of Pb(II) ions onto the bone samples at 25˚C.

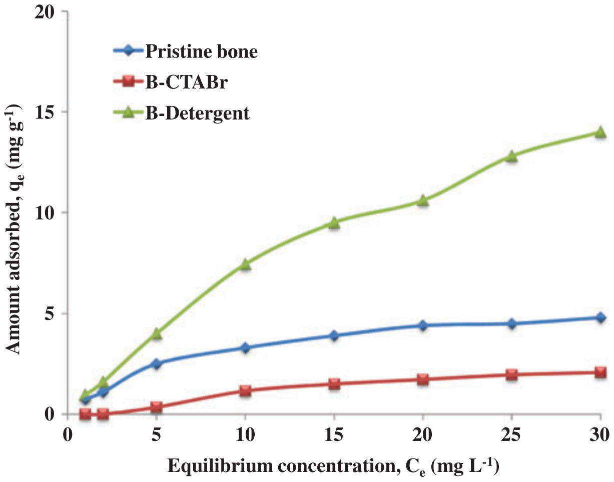

Fig. 12. The effect of initial concentrations for the adsorption of Hg(II) ions onto the bone samples at 25˚C.

3.7.3. Effect of adsorbent dosage

The adsorbent dosage is one of the important factors because it presents the capacity of the adsorbent for a given initial concentration of the adsorbate. To determine the relation of Pb(II) sorption on adsorbent dosage, various dosages (0.02–0.5 g) of bone, at a controlled temperature of 25 ± 1˚C, were added into 10 mL of 9 mg L^{-1} Pb(II) solution without any changes on the solution pH. The relation between the adsorbent dosage and removal percentage of Pb(II) by the pristine bone and B-Detergent is shown in Fig. 13. Fig. 13 shows that the removal percentage of Pb(II) increased with increasing the adsorbent dosage due to increase in the number of adsorption sites [15,24]. As the adsorbent dosage increased from 0.02 to 0.1 g, the removal efficiency of Pb(II) ions increased significantly from 12.44 to 70% and 45 to 88% for pristine bone and B-Detergent, respectively. It is apparent that removal efficiency of Pb(II) ions is increased by cleaning process with detergent where Pb(II) ions were removed up to 95% by B-Detergent. The removal efficiency of Pb(II) ions by B-Detergent after 0.1 g of sorbent dosage was negligible because it achieved the equilibrium adsorption capacity at higher adsorption dosages [15,24]. Therefore, 0.1 g of adsorbent dosage was chosen as the optimal dosage for the rest of the study.

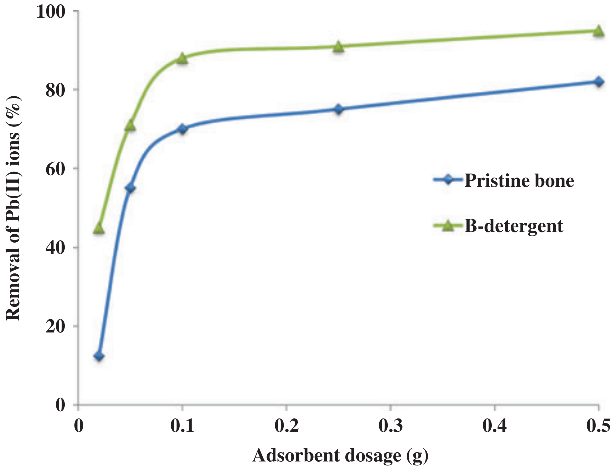

Fig. 13. Effect of adsorbent dosage on the sorption of Pb (II) ions by the bone samples from aqueous solution.

3.7.4. Adsorption isotherms

The equilibrium adsorption isotherms are known as one of the most important data to understand the mechanism of the adsorption and describe how adsorbates interact with adsorbents [49]. The experimental adsorption equilibrium data of HMs on the bone samples were fitted by applying the Langmuir, Freundlich, and Langmuir–Freundlich isotherm models, which are usual models for aqueous-phase adsorption [48]. These adsorption models give a representation of the adsorption equilibrium between an adsorbate in solution and the surface active sites of the adsorbent. The Langmuir, Freundlich, and Langmuir–Freundlich adsorption isotherms can be expressed by Eqs. (2)–(4), respectively.

$$q_e = \frac{K_L q_m C_e}{(1 + K_L C_e)} \tag{2}$$

$$q_e = K_F C_e^{1/n} \tag{3}$$

$$q_e = \frac{K_L q_m C_e^{1/n}}{\left(1 + K_L C_e^{1/n}\right)} \tag{4}$$

where q_e (mg g^{-1}) is the specific equilibrium amount of adsorbate, C_e (mg L^{-1}) is the equilibrium concentration of adsorbate, q_m is the maximal adsorption capacity, and K (K_L and K_F) (L mol^{-1}) and n are empirical constants, indicative of the extent of adsorption and the adsorption effectiveness, respectively. The constant n gives an idea of the grade of heterogeneity in the energetic centers distribution and is related to the magnitude of the adsorption driving force [48]. High values on n indicate a relative uniformity in the surface. Low values of n in isotherms mean high adsorption at low concentrations in the dissolution. Furthermore, low values of n indicate the existence of a great proportion of active sites with a high energy.

Langmuir equation relates the coverage of molecules on a solid surface to the concentration of a medium above the solid surface at a fixed temperature. Adsorption is limited to monolayer coverage and intermolecular forces decrease with the distance from the adsorption surface. On the other hand, the Freundlich model supposes that the adsorption surface is heterogeneous, that interactions among adsorbed molecules can occur, and that multilayer adsorption is possible. The Langmuir, Freundlich, and Langmuir–Freundlich adsorption isotherms exhibit an approximately linear relationship for all the bone samples. The data obtained from the modified bone systems revealed that Langmuir and a combination of the Langmuir and Freundlich (L–F) isotherm models fitted the experimental data better ($R^2 > 0.994$) than Freundlich isotherm ((Table 2)). Therefore, it is realistic to infer that the adsorption active sites on the modified ostrich bone are energetically heterogeneous (non-uniform surfaces) [52], and this is a major aspect in this model. The maximum adsorption capacity (q_m) obtained by L–F isotherm for Pb(II) (91.51 mg g^{-1}) was much higher than the values found for Hg(II) (38.02 mg g^{-1}) onto the B-Detergent and it also suggests that there is a high thermodynamic stability for Pb(II) immobilized on the active sites of the B-Detergent (Table 2). The maximum adsorption capacity (q_m) for Pb(II) decreased in the following order: B-Detergent > Pristine bone > B-CTABr.

3.7.5. Adsorption kinetics

The effect of shaking time (0–360 min) on the adsorption of Pb(II) (9 mg L^{-1}) and Hg(II) (5 mg L^{-1}) ions onto B-Detergent (0.1 g), in the solution of pH 6.5 at 25°C was shown in Figs. 14 and 15, respectively. It is easily seen that the amount of adsorption increased with increasing the contact time. Studies conducted on the adsorption kinetics of Pb(II) and Hg(II) removal revealed that the majority of Pb (91.9%) and Hg (87.7%) was removed within the first 0–60 min contact with the modified bio-adsorbent. However, the initial rapid adsorption gives away a very slow approach to equilibrium. In fact, the fast adsorption at the initial stage is probably due to the increased concentration gradient between the adsorbate in solution and adsorbate in

Table 2
Fitting of the parameters of the experimental results to the Langmuir, Freundlich, and Langmuir–Freundlich equation parameters

	q_m	K_L	K_F	n	R^2	Sorption model
Pristine bone						
Pb(II)	10.48	1.01×10^{-1}			0.9733	Langmuir
			0.140	0.366	0.9307	Freundlich
	7.31	7.13×10^{-2}		0.6726	0.991	Langmuir–Freundlich
Hg(II)	6.99	2.45×10^{-2}			0.9677	Langmuir
			0.140	0.366	0.9307	Freundlich
	5.36	4.4×10^{-2}		0.966	0.9862	Langmuir–Freundlich
B-CTABr						
Pb(II)	9.35	19.72×10^{-3}			0.8371	Langmuir
			0.068	0.883	0.8268	Freundlich
	3.412	1.27×10^{-3}		0.307	0.9982	Langmuir–Freundlich
Hg(II)	7.91	3.62×10^{-2}			0.9726	Langmuir
			0.048	0.651	0.7143	Freundlich
	4.98	1.56×10^{-3}		1.09	0.9832	Langmuir–Freundlich
B-Detergent						
Pb(II)	89.44	11.13×10^{-3}			0.9942	Langmuir
			0.306	0.477	0.9859	Freundlich
	91.51	11.1×10^{-3}		1.043	0.9960	Langmuir–Freundlich
Hg(II)	33.33	1.85×10^{-2}			0.9934	Langmuir
			0.196	0.477	0.9448	Freundlich
	38.02	1.72×10^{-2}		1.037	0.9937	Langmuir–Freundlich

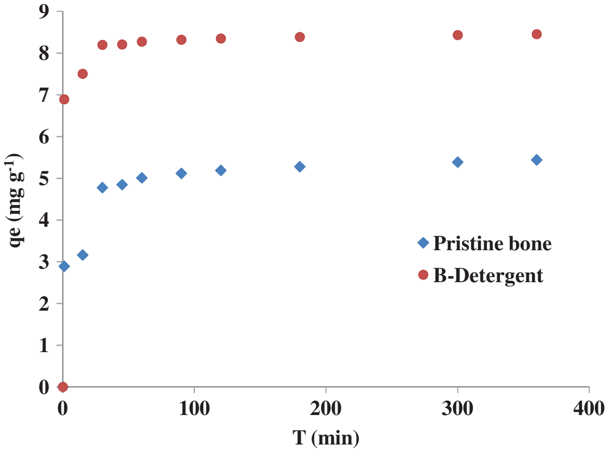

Fig. 14. The adsorption kinetics of the pristine bone and B-Detergent for Pb(II) ions at room temperature.

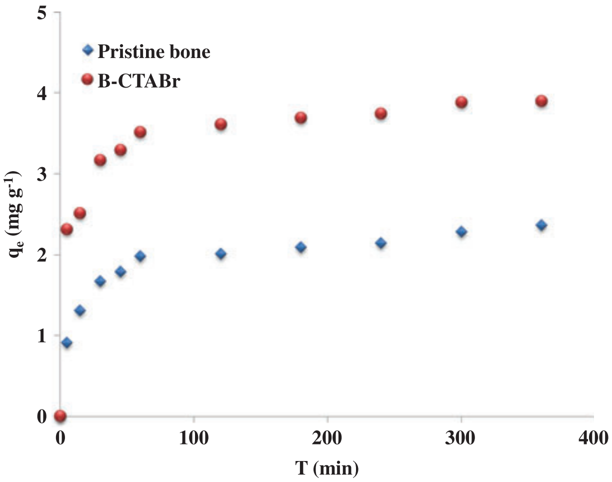

Fig. 15. The adsorption kinetics of the pristine bone and B-Detergent for Hg(II) ions at room temperature.

adsorbent as there must be increased number of vacant active sites available in the beginning [24,48].

In order to determine and interpret the mechanisms of metal adsorption processes and major parameters governing sorption kinetics, kinetic sorption data obtained empirically were fitted to the pseudo-first-order, pseudo-second-order, and intraparticle diffusion models shown as Eqs. (5)–(7). Each of them has been widely used to describe metal and organic sorption on different sorbents [22,23,48]. From the linear form of these three models, equations can be written as follows:

$$\text{Pseudo-first-order equation}: \; q_t = q_e[1 - \exp(-k_1 t)] \quad (5)$$

$$\text{Pseudo-second-order equation}: \; q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (6)$$

$$\text{Intraparticle diffusion equation}: \; q_t = k_{\text{int}} t^{0.5} \quad (7)$$

The initial adsorption rate (h) can be determined from k_2 and q_e values [22]. Using:

$$h = k_2 q_e^2 \quad (8)$$

where k_1, k_2, and k_{int} are the adsorption rate constants of first-, second-order kinetic, and intraparticle diffusion models, in min^{-1}, $\text{L mg}^{-1}\,\text{min}$, and $\text{mg g}^{-1}\,\text{min}^{-1/2}$, respectively; q_e and q_t in mg g^{-1}, are equilibrium adsorption uptake (at time $t = \infty$) and adsorption uptake (at time t), respectively.

The calculated kinetics parameters for adsorption of Pb(II) (at initial concentration of $10\ \text{mg g}^{-1}$) and Hg(II) (at initial concentration of $5.0\ \text{mg g}^{-1}$) onto the B-Detergent, are tabulated in Table 3. As can be observed, the pseudo-second-order equation appeared to be the best-fitting model than those for the other two equations (the correlation coefficient is extremely high for the pseudo-second-order equation of B-Detergent; $R^2 > 0.99$). Similar results have been reported about the adsorption of HMs onto the different adsorbents in the literature [22–24,48].

The pact of the experimental data with the pseudo-second-order kinetic model (the pseudo-second-order equation is based on the sorption capacity on the solid phase) indicates that the adsorption of HMs onto the modified bone may be considered to composed of two processes with initial adsorption rate of 5.28 for Pb and 0.29 for Hg over B-Detergent. The adsorption rate was related to the content and type of active adsorption site on the matrix of adsorbent).

3.7.6. *Effect of the temperature on the uptake*

Furthermore, the equilibrium adsorption capacity of Pb(II) and Hg(II) ions onto the favored adsorbent, B-Detergent, was studied at higher temperatures of 50 and 80℃ in pH 6.5 (Figs. 16 and 17). The increase in the temperature of solutions of Pb(II) and Hg(II) from 25 to 50℃ and 80℃ leads to an increase in the adsorption capacity of the bone samples. This may indicate that adsorption of metal cations on active sites of the bone samples are endothermic and may be elucidated by availability of more active sites of adsorbent, the enlargement and activation of the adsorbent surface at higher temperatures. This may also be due to the easily mobility of metal cations from the bulk solution toward the adsorbent surface and enhanced the accessibility to the active sites [15,16,23].

In order to better understand the effect of rising temperature on the adsorption of the HMs ion onto the active sites of the pristine bone and B-Detergent, three basic thermodynamic parameters were studied: the Gibbs free energy of adsorption (ΔG°), the enthalpy change (ΔH°), and the entropy change (ΔS°).

The thermodynamic parameters ΔG°, ΔS°, and ΔH° for this adsorption process were determined using following equations [15,16].

$$\Delta G^\circ = -RT \ln K \quad (9)$$

where K is the thermodynamic equilibrium constant. The values of K can be determined by plotting $\ln(q_e/C_e)$ against q_e and extrapolating to zero, where q_e is the adsorbed metal ions concentration at equilibrium and C_e is the equilibrium concentration of metal ions in solution. The effect of temperature on thermodynamic constant was determined by Eq. [23]:

$$\mathrm{d}\ln K/\mathrm{d}t = \Delta H^\circ/RT^2 \quad (10)$$

The ΔH° and ΔS° values were calculated from slope and intercept of the linear plot, of $\ln K$ vs. $1/T$.

$$\ln K = \Delta S^\circ/R - \Delta H^\circ/RT \quad (11)$$

and Gibbs free energy is given by Eq. (12), where ΔG° is the free energy change (J mol^{-1}); R and T are the universal constant ($8.314\ \text{J mol}^{-1}\,\text{K}$) and the absolute temperature (K), respectively.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (12)$$

The corresponding values of thermodynamic parameters are presented in Table 4. This shows that ΔH and ΔS are positive for all the experiments and ΔG is negative in most systems. The positive values of ΔH° revealed that the adsorption process was endothermic in nature; hence with increasing temperature the adsorbed amount at equilibrium increased.

The positive value of ΔS° revealed the increased randomness and an increase in the degrees of freedom at the solid-solution interface during the immobilization of the Pb(II) and Hg(II) ions on the active sites of the adsorbent, which indicate the partial dehydration of the metal ions before adsorption (liberation of water

Table 3
Kinetic parameters for the adsorption of Pb(II) and Hg(II)

	First-order model			
System	k_1 (min^{-1})	q_1 (mg g^{-1})		R^2
Pristine bone				
Pb(II)	0.712	4.878		0.611
Hg(II)	7.724	2.169		0.815
B-Detergent				
Pb(II)	0.196	8.196		0.549
Hg(II)	4.318	3.184		0.833
	Second-order model			
	k_2 (g (mg^{-1}min))	q_2 (mg g^{-1})	h (mg (g^{-1} min))	R^2
Pristine bone				
Pb(II)	0.029	5.525	0.894	0.999
Hg(II)	0.028	2.375	0.161	0.996
B-Detergent				
Pb(II)	0.072	8.547	5.289	1
Hg(II)	0.023	3.546	0.2944	0.997
		Inter-particle model		
		K_{int} (mg (g^{-1}min$^{1/2}$))		R^2
Pristine bone				
Pb(II)		0.127		0.644
Hg(II)		0.069		0.816
B-Detergent				
Pb(II)		0.076		0.565
Hg(II)		0.088		0.829

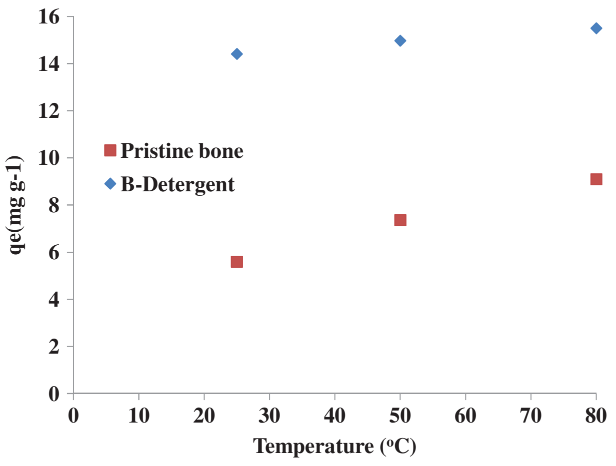

Fig. 16. Effect of temperature on the adsorption of Pb(II) ions onto the bone samples.

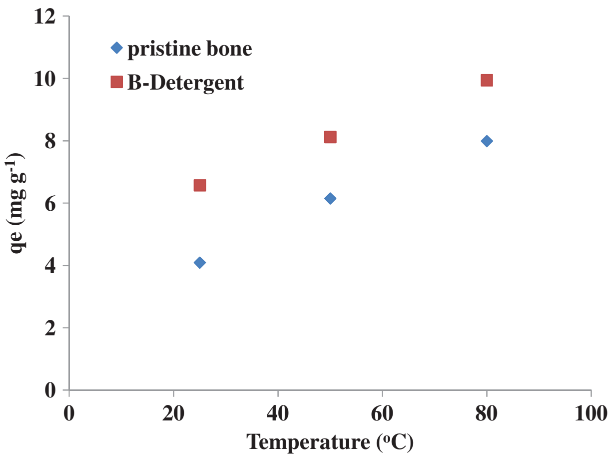

Fig. 17. Effect of temperature on the adsorption of Hg(II) ions onto the bone samples.

Table 4
Thermodynamic parameters for the adsorption of Pb(II) and Hg(II) onto the bone samples

System	ΔH° (kJ mol^{-1})	ΔS° (J mol^{-1} K)	T (K)	ΔG° (kJ mol^{-1})
Pristine bone				
			298	1.526
Pb(II)	14.246	42.683	323	0.459
			353	−0.821
			298	2.591
Hg(II)	13.643	41.231	323	1.386
			353	−0.059
B-Detergent				
			298	−5.319
Pb(II)	19.604	83.638	323	−7.410
			353	−9.920
			298	0.938
Hg(II)	16.951	48.187	323	−0.127
			353	−1.406

molecules of hydrated-M(II)) and either the adsorbed solvent molecules that were released by the adsorbate, therefore, enabling commonness of randomness and spontaneity in the system [53]. The necessity of a large amount of heat to remove the bivalent metal ions from the solution makes the sorption process endothermic. The highest ΔS° (disorder of the system) was observed in case of Pb(II) onto B-Detergent, which indicates that Pb(II) ion lose most of their water of solvation. This is also supported by the positive value of ΔH, in fact, the positive value of the standard enthalpy change for Pb (II) and Hg(II) ions sorption onto B-Detergent are 19.604 and 16.951 kJ mol^{-1}, respectively, indicates endodermic nature of adsorption and an ion exchange type mechanism [53].

It was also observed that with increase in temperature the value of ΔG decreases, which indicated that sorption processes was spontaneous and thermodynamically favorable by an increase in temperature (Table 4). In fact, the value of ΔG° for physisorption is in the range $-20 < \Delta G^\circ < 0$ kJ mol^{-1}, but chemisorption is between $-400 < \Delta G^\circ < -80$ kJ mol^{-1} [53]. The calculated ΔG° values based on Eq. (12) for the adsorption of Pb(II) and Hg(II) ions onto the bone samples were in the range of physisorption (Table 4).

3.8. Economical discussion

Iran has arid and semi-arid climates that is mostly characterized by low rainfall and high potential evapotranspiration. This country is approaching to face water stress and it is predicted that faces an extreme water scarcity in 2025. On the other hand, rapid urbanization and industrialization have increased not only water demand but also water pollution. Water pollution by urban and industrials wastewater with metal ions is a matter of environmental concern in Iran. Iran will suffer a serious environmental degradation unless an adequate environmental management is applied. In order to combat water pollution, proper effluent treatment systems must be used. One of the useful solutions to such a problem is adsorption process with high efficiency, approximately low cost and readily availability of different adsorbents. Selection of an adsorbent is very important for the use of adsorption process as a treatment technique. The comparative price of the biological origin material used in the present study is very much lower than that of commercial adsorbent (i.e. activated carbons or ion exchange resins). The ostrich bone waste and laundry detergent are available with low price, reproducible without the need of high technology equipment, and after considering expenses like transport; chemicals modification (treatment with laundry detergent), and processing cost, the cost of the modified ostrich bone would be approximately US$ 100 ton^{-1}. The cost of the activated carbon used for wastewater treatment in our country is around US$ 1,100 ton^{-1}. In spite of the extra processing cost required for B-Detergent synthesis in commercial level, but improved adsorption capacities may compensate the cost for such a process. Also, the price of such a process may decrease, as more industries consider their use for treating metal contaminated wastewater. From practical point of view, this adsorbent may be used as a filter for drain pipes, material for permeable reactive barrier and impermeable layer under the landfills. Moreover, Detergent is inexpensive and seemingly easy to yield in large quantities, so offering the occasion to utilize this bioadsorbent in third world drinking wastewater purification in order to reduce the poisoning and suffering of millions of people worldwide.

4. Conclusions

The results showed that the pristine ostrich bone has the low capacity to adsorb Pb(II) and Hg(II) ions from the wastewater. Pristine ostrich bone contains more than 80% organic compounds which could block the inorganic phase and suitable active sites of the bone. So in this work the pretreatment of pristine ostrich bone with common surfactants (as cetyltrimethylammonium bromide (cationic surfactant) and laundry detergent (anionic surfactant)) was found to improve the biosorption efficiency. The results obtained in this study prove that the heterogenized laundry detergent over ostrich bone waste can be prosperously used for the removal of Pb(II) and Hg(II) ions from aqueous solutions. The presence of CTABr and laundry detergent on the ostrich bone was verified by FTIR, XRD, BET, SEM, and EDX analyses. SEM images and BET surface area have revealed that laundry detergent-treated have superior porosity and enhanced surface area than CTABr-treated. The kinetic data indicates that the pseudo-second-order kinetic model was found to be well suited and provide high degree of correlation with the experimental data for the adsorption process of HMs on B-Detergent. On the other hand, the increase in adsorption capacity of B-Detergent than B-CTABr may be attributed to the improved surface hydrophobicity of ostrich bone waste with Detergent and either increasing accessibility of the adsorbent active sites. It was further shown that the adsorption process was spontaneous and endothermic in nature. The results offer a versatile and mild method for immobilization of surfactant on the surface of a biological origin support (ostrich bone), for the first time, which significantly improved the adsorption capacity of the animal bone toward HMs from aqueous solution. Furthermore, the chemical modification of ostrich bone with surfactants removed most of the fat tissues and organic compounds which already blocked the active sites and inorganic phase of the bone and further enhanced the adsorbent properties, such as selectivity and adsorption capacity.

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