RESEARCH ARTICLE

Nanohydroxyapatite and its polycaprolactone nanocomposite for lead sorbent from aqueous solution

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ABSTRACT

Objective(s): Lead is a very strong poison in the environment. Lead toxicity can be affected on the human body and caused disease. Therefore, the design of lead sorbent can be had the great help to the medical field. In this work, the nanohydroxyapatite (n-HA) was used for lead absorption from aqueous solution. Then, polycaprolactone (PCL) nanocomposite was modified with n-HA by simple preparation method as lead sorbent.
Methods: The samples were characterized by X-ray diffraction (XRD) analysis, field emission scanning electron microscope (FE-SEM), BET surface area, and Ultraviolet–visible (UV–Vis) spectroscopy. The effect of parameters including pH and temperature of solution, amount and concentration of sorbent was investigated on lead absorption.
Results: FE-SEM results confirmed that the samples are in nano scale. The lead absorption was approved by UV–Vis spectroscopy and BET surface area. The absorption value was increased by increase of concentration, pH, and temperature.
Conclusions: This work focuses on preparing an efficient lead sorbent system based on nanohydroxyapatite and its polycaprolactone nanocomposite. The results indicate that this nanocomposite can have a good potential to develop different adsorbents.

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INTRODUCTION

Water is one of the most important natural sources in the world for the survival of all living beings and the development of humans. The water pollution with heavy metal is becoming a more serious problem of the economic development and rapid industrialization from recent years [1, 2]. Lead is the most important heavy toxic metal in the environment. The lead nature is non-biodegradable pollutant with detrimental effects on human health [3]. This element tends to accumulate in living organisms and leads to serious illnesses [4]. Lead absorption has become a global challenge due to the widespread use of lead metal in various industrials [5, 6].

Nanotechnology has attracted a great attention because of unique properties of nanomaterials and nanostructures [7] in various fields such as drug delivery [8-10], antibacterial activity [11-13], food packaging [14, 15], energy [16], sensor [3], agriculture [17], dental [18], absorption of hazardous material [19, 20], and etc. Various methods have been developed to remove heavy metals from water such as chemical precipitation [21], ion exchange [22], reverse osmosis [23], and adsorbent [24]. Recently, adsorbent nanomaterial was applied for the removal of lead from aqueous solutions [25, 26]. Easy separation of sorbent from the water is expanding as beneficial and functional

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properties for absorption of heavy metals. Therefore, it is important to develop the use of adsorbents based on magnetic [27-30] and polymer [27, 31] materials. In the recent years, hydroxyapatite polymer composite was used to lead(II) uptake from aqueous solutions [32]. Hydroxyapatite is a mineral porous material and it can be acted as sorbent of lead ions [33]. Polycaprolactone is one of the most commonly-used polymers for the removal of hazardous, carcinogenic, and toxic pollutants of heavy metals from aqueous solutions. According to previous report, polycaprolactone nanofibrous materials were modified by clay and zeolite nanoparticles for lead adsorption [34]. Also in another report, cyclodextrin-polycaprolactone titanium dioxide nanocomposites were used as a sorbent for the removal of lead in aqueous waste [35]. In present study, nanohydroxyapatite/polycaprolactone nanocomposites were prepared by a simple method and lead absorption was investigated by nanohydroxyapatite and n-HA/PCL nanocomposites from aqueous solution.

MATERIALS AND METHODS

Materials

All chemicals were analytical grade. Ultra-pure water was used for the preparation of all reagents solutions. Lead acetate salt and poly (ε-caprolactone) (with 1400 g/mol molecular weight) were purchased from Merck company (Germany), and nanohydroxyapatite bought from Pardis Pajoohesh Fanavaran-e Yazd company (Iran).

Methods

PCL nanocomposites were prepared by solution casting method with different percentages of nanohydroxyapatite. PCL and n-HA were dissolved in chloroform solvent and kept stirring for 30 min at 40 ˚C. The n-HA powder was placed to ultrasonic bath for better dispersion. Then nanohydroxyapatite solution was added to PCL solution under magnetic stirring system. The final solution was transferred to the plate and allowed to dry. PCL nanocomposites with 5 and 10 percentage of n-HA were shown better results for lead absorption.

Characterization

The crystalline structure of sample was investigated by X-ray diffraction utilizing Cu Kα X-ray radiation with a voltage of 40 kV and a current of 30 mA by X'pert pro diffractometer (X' Pert Pro model, Panalytical, Peru). Field emission scanning electron microscope was employed to observe morphology and size (Sigma VP model, ZEISS, Germany). The surface area was determined using nitrogen gas sorption by n-HA samples at 298 K and 0.88 atmosphere pressure (BElSORP Mini model, Microtrac Bel Corp, Japan). Lead absorption was evaluated by UV–Vis spectroscopy (GENESYS 30 model, Thermo Scientific, America).

RESULTS AND DISCUSSION

XRD

The XRD pattern of samples was measured in 2θ range 5-80° that used to identify the crystalline structure (Fig. 1). X-ray diffraction patterns were showed characteristic peaks between 2θ range from 30 to 40° according to the previous reports [36, 37]. The crystal structural of n-HA has been preserved after lead absorption. The XRD of PCL approved two characteristic peaks of the crystalline structure according to the previous report [38]. Due to the high percentage of polymer in the nanocomposite, characteristic peaks of nanohydroxyapatite were not observed.

FE-SEM

The FE-SEM images were shown for n-HA before and after lead adsorption and n-HA/PCL nanocomposite (Fig. 2). According to the results, nanohydroxyapatite had needle-like morphology and the particle size was estimated to be 50 (before lead adsorption) and 80 nm (after lead adsorption). Lead absorption was caused the increase of particle size due to phenomenon of swelling. The FE-SEM of n-HA/PCL nanocomposite was shown in the form of image from the cross section. This result presented for the first time.

BET

The Brunauer–Emmett–Teller (BET) analysis was used for determination of surface area of nanohydroxyapatite by N_2 adsorption before and after lead absorption (Fig 3). Based on the results, the surface area of n-HA decreased with lead adsorption from 89.966 m^2/gr to near-zero. In fact, lead approximately filled up the pores and there is not any residual porosity.

UV–Vis spectroscopy

The lead absorption was investigated by UV–Vis spectroscopy. The calibration curve of lead was

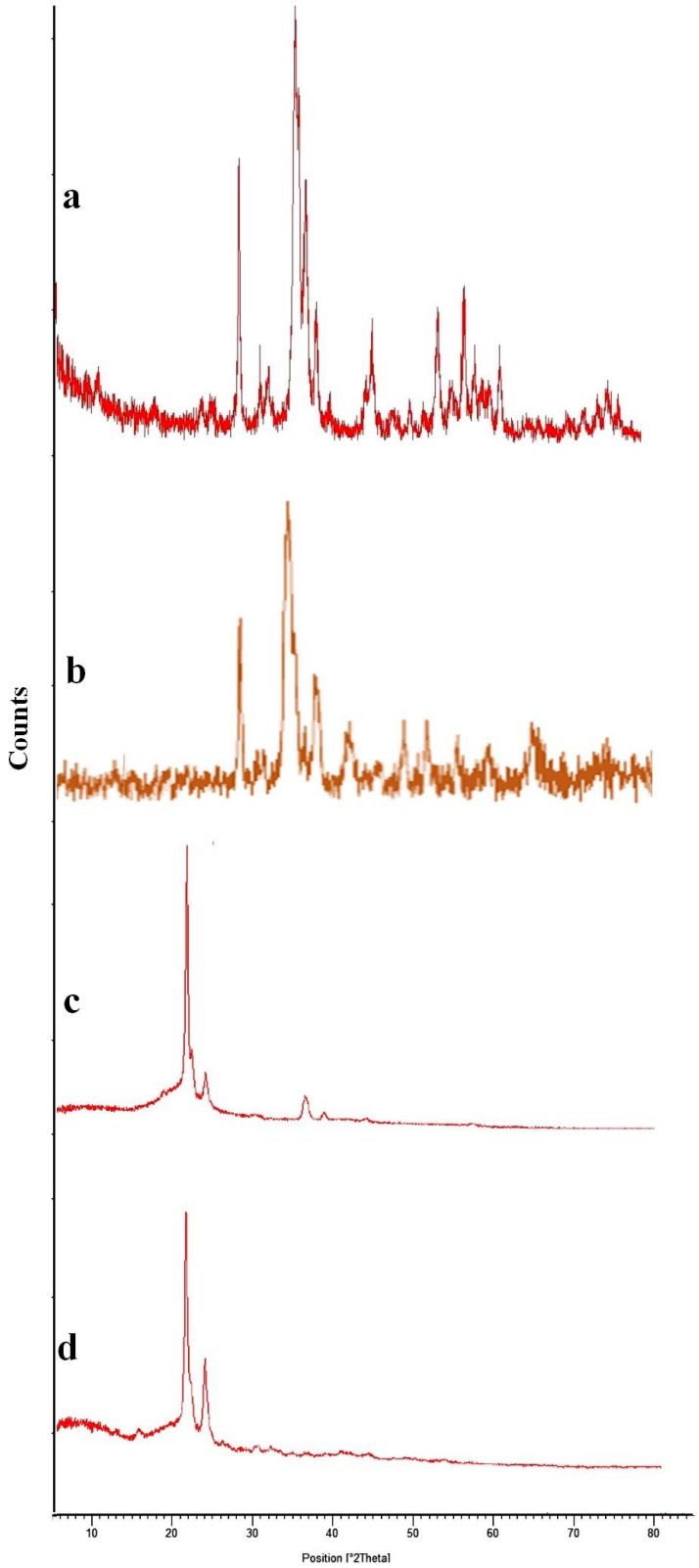

Fig. 1. XRD Pattern of a) n-HA, b) n-HA after lead adsorption, c) PCL polymer, and d) n-HA/PCL nanocomposite.

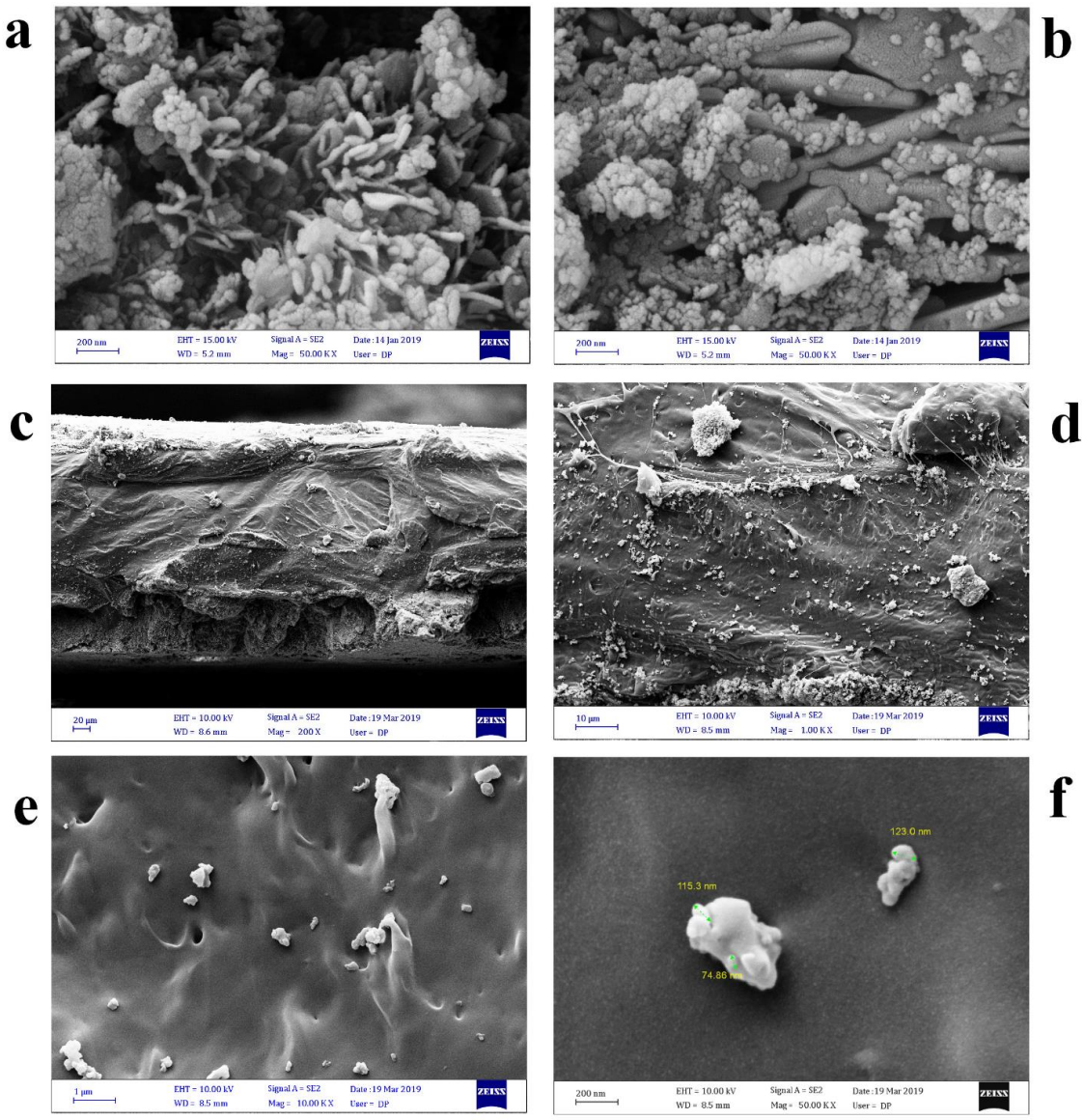

Fig. 2. FE-SEM images of n-HA a) before and b) after lead adsorption, cross section image of n-HA/PCL nanocomposite c) in 20 µm, d) 10 µm, e) 1 µm, and f) 200 nm scale bare.

examined at λ_{max} = 208 nm with concentration of 5, 10, 20, 30, and 40 ppm (Fig 4. a). The adsorption diagram was investigated at different n-HA amounts including 0.1, 0.25, and o.5 g with a constant concentration of 250 ppm of lead at different times (Fig 4. B). Based on the results, increase of sorbent amount was resulted to increase of adsorption due to increase of surface area.

The absorption was evaluated in different lead concentrations including 50, 80, 100, 150, and 250 ppm by n-HA and n-HA/PCL nanocomposite at different times (Fig. 5). In general, the increase of concentration was resulted to increase of lead adsorption. The nanocomposites were examined with two concentrations of lead including 100 and 250 ppm. Based on nanocomposite results, the increase of percentage had higher effect on the increase of lead adsorption than the increase of concentration. Also, high concentrations were resulted to increase of inhibition and decrease of absorption.

Lead adsorption was studied in various pH

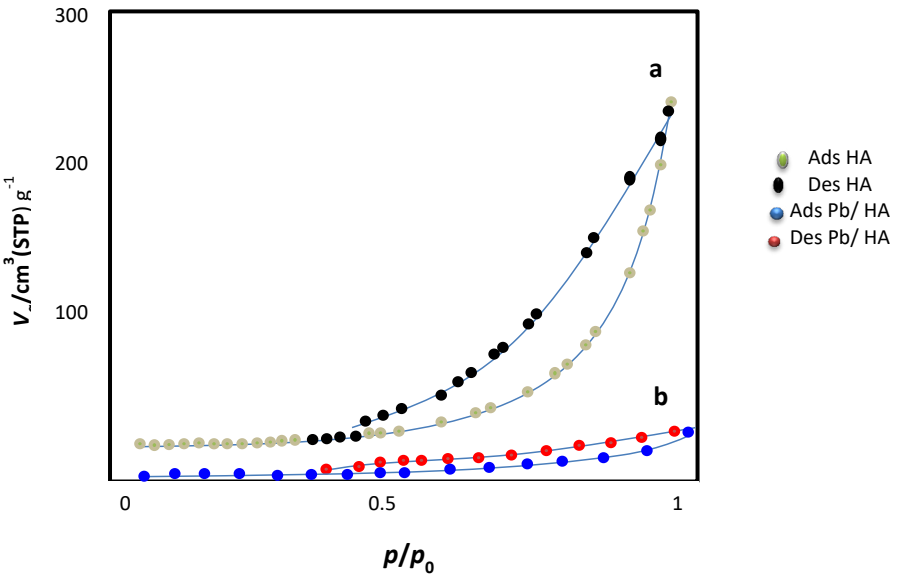

Fig. 3. The absorption/desorption N_2 curve related to n-HA a) before and b) after lead adsorption.

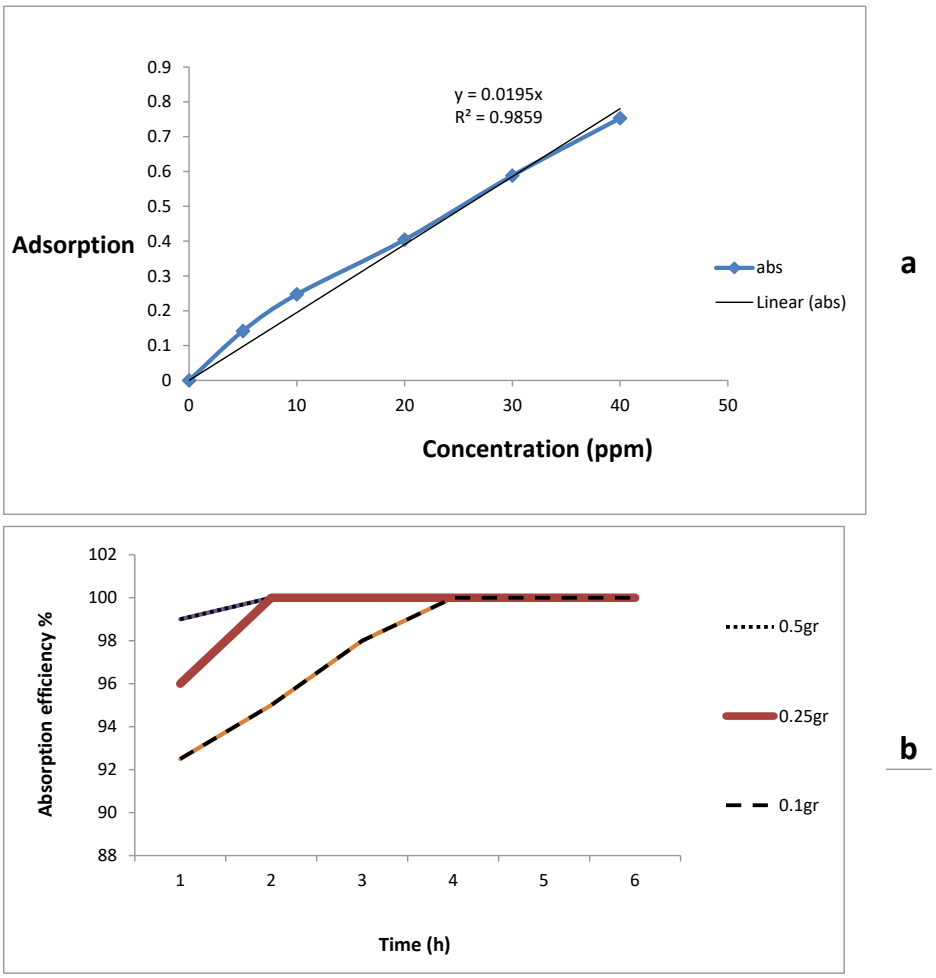

Fig. 4. a) The calibration curve of lead and b) the diagram of lead adsorption in different n-HA amounts.

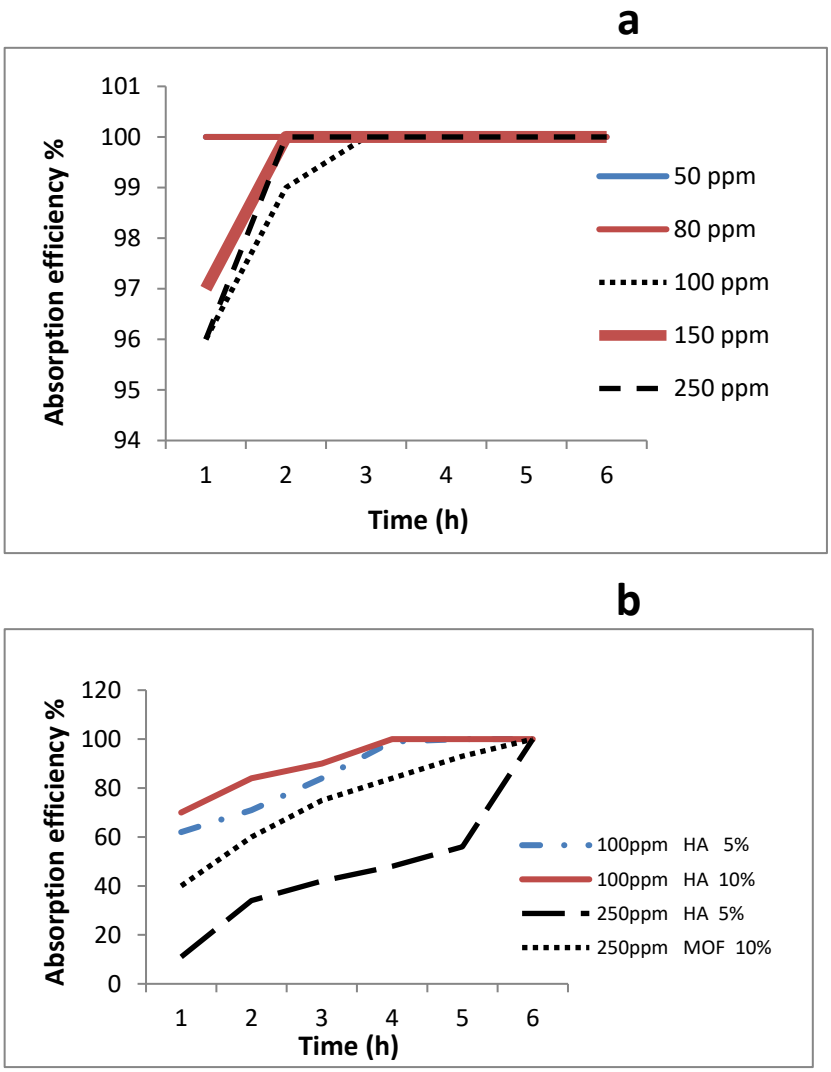

Fig. 5. The diagram of lead adsorption by a) n-HA and b) n-HA/PCL nanocomposite in different lead concentrations.

of solution including acidic (pH=2), neutral, and basic (pH=10) for 0.25 g n-HA with 250 ppm of lead concentration and 10% nanocomposite with 100 ppm of lead concentration (Fig. 6). The higher pH was caused more surface active sites, decrease of competition between positive charges, and increase lead adsorption through the electrostatic force of attraction. The result is according to the previous reports [5, 37].

Lead adsorption was studied in different temperature including 25 (ambient), 40, 60, and 80 °C for 0.25 g n-HA with 250 ppm of lead concentration and 10% nanocomposite with 100 ppm of lead concentration (Fig. 6). Based on the result, the increase of temperature was resulted to increase of lead adsorption because of kinetic energy and Brownian motion. According to the previous report, temperature is directly related to the potential of lead adsorption by sorbent [37].

CONCLUSIONS

In this research, n-HA and n-HA/PCL nanocomposite were used for lead adsorption. The effect of different parameter including pH and temperature of solution, amount and concentration of sorbent was shown on lead adsorption by n-HA and its nanocomposite. The results presented that n-HA and n-HA/PCL nanocomposite can represent

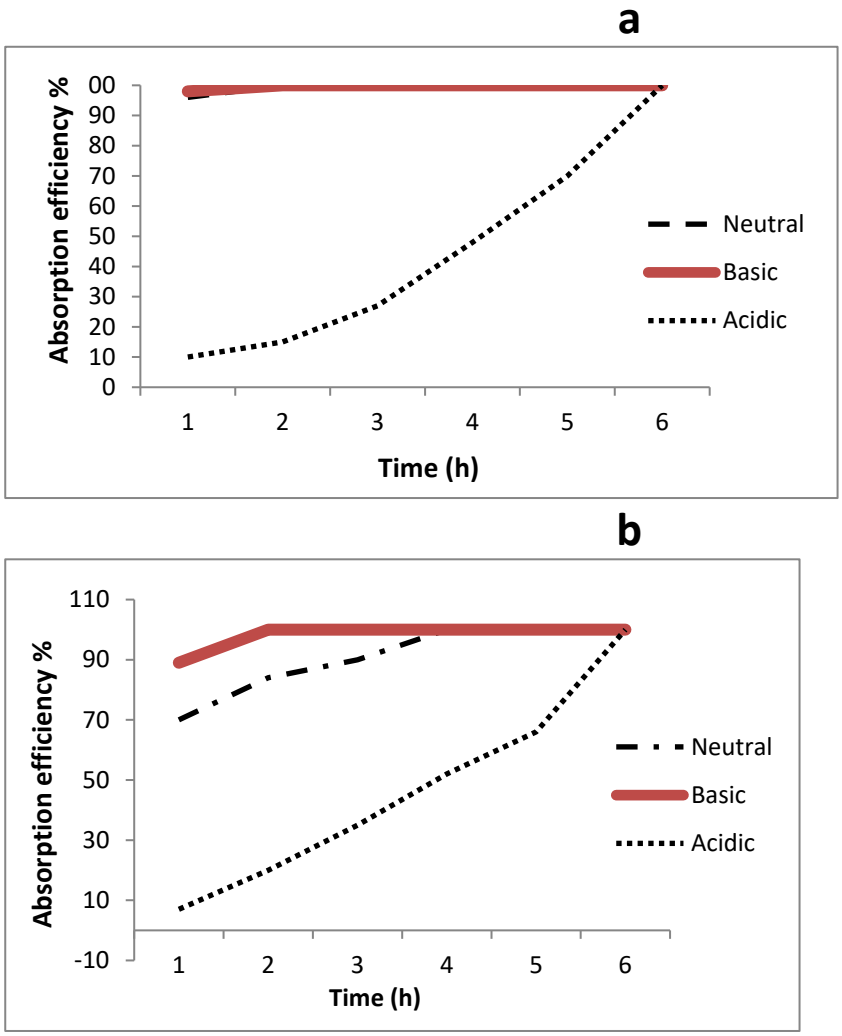

Fig. 6. The diagram of lead adsorption by a) n-HA and b) n-HA/PCL nanocomposite in different pH.

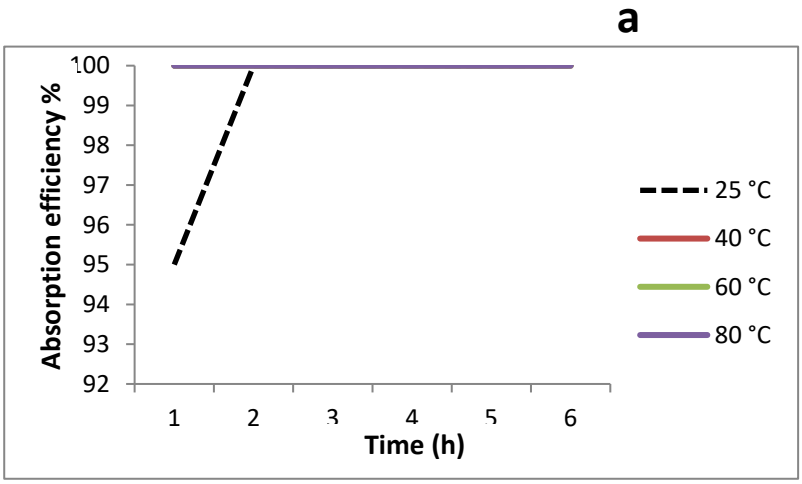

Fig. 7. The diagram of lead adsorption by a) n-HA and b) n-HA/PCL nanocomposite in different temperature.

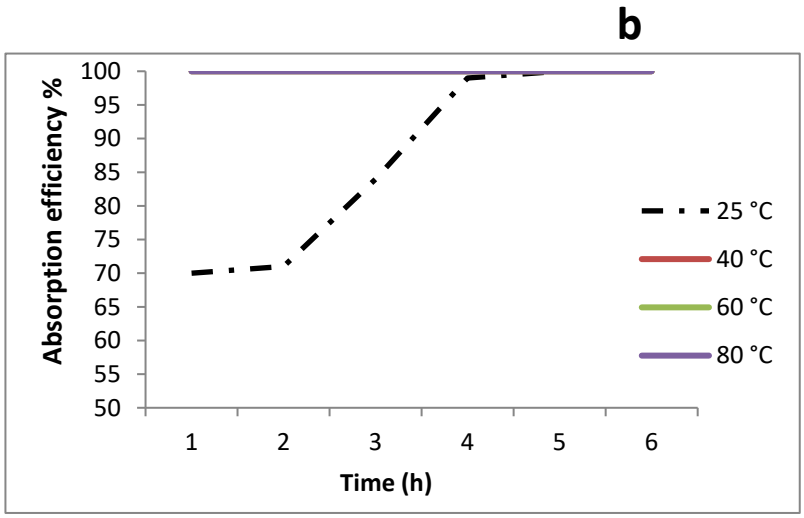

Fig. 7. The diagram of lead adsorption by a) n-HA and b) n-HA/PCL nanocomposite in different temperature.

an economical source of lead sorbent from aqueous solution to develop environmental applications. The future prospects can be developed great application of this nanocomposites to pharmaceutical and medical.

CONFLICT OF INTERST

The authors report no conflict of interest.

REFERENCES

1. Tchounwou PB, Yedjou CG, Patlolla AK, Sutton DJ. Heavy Metal Toxicity and the Environment. Experientia Supplementum: Springer Basel; 2012. p. 133-64.
2. Cheraghi M, Lorestani B, Yousefi N. Effect of Waste Water on Heavy Metal Accumulation in Hamedan Province Vegetables. International Journal of Botany. 2009;5(2):190-3.
3. Adabi M. Detection of lead ions using an electrochemical aptasensor. Nanomed Res J. 2019;4(4):247-252.
4. Latif Wani A, Ara a, Ahmad Usmani J. Lead toxicity: a review. Interdiscip Toxicol. 2015; 8(2):55–64.
5. Iconaru S, Motelica-Heino M, Guegan R, Beuran M, Costescu A, Predoi D. Adsorption of Pb (II) Ions onto Hydroxyapatite Nanopowders in Aqueous Solutions. Materials. 2018;11(11):2204.
6. González-Muñoz MJ, Rodríguez MA, Luque S, Álvarez JR. Recovery of heavy metals from metal industry waste waters by chemical precipitation and nanofiltration. Desalination. 2006;200(1-3):742-4.
7. Hajiashrafi S, Motakef Kazemi N. Preparation and evaluation of ZnO nanoparticles by thermal decomposition of MOF-5. Heliyon. 2019;5(9):e02152.
8. Motakef-Kazemi N, Shojaosadati SA, Morsali A. In situ synthesis of a drug-loaded MOF at room temperature. Microporous and Mesoporous Materials. 2014;186:73-9.
9. Motakef-Kazemi N, Shojaosadati SA, Morsali A. Evaluation of the effect of nanoporous nanorods Zn2(bdc)2(dabco) dimension on ibuprofen loading and release. Journal of the Iranian Chemical Society. 2016;13(7):1205-12.
10. Miri B, Motakef-Kazemi N, Shojaosadati SA, Morsali A. Application of a nanoporous metal organic framework based on iron carboxylate as drug delivery system. Iran J Pharm Res. 2018;17(4):1164–1171.
11. Adibzadeh P, Motakef-Kazemi N. Preparation and characterization of curcumin-silver nanoparticle and evaluation of the effect of poly ethylene glycol and temperature. J Nanoanalysis. 2018;5(3): 156-162.
12. Hajiashrafi S, Motakef-Kazemi N. Green synthesis of zinc oxide nanoparticles using *parsley* extract. Nanomed Res J. 2018;3(1):44-50.
13. Feizi Langaroudi N, Motakef-Kazemi N. Preparation and characterization of O/W nanoemulsion with Mint essential oil and Parsley aqueous extract and the presence effect of chitosan. Nanomed Res J. 2019;4(1):48-55.
14. Sharma C, Dhiman R, Rokana N, Panwar H. Nanotechnology: An Untapped Resource for Food Packaging. Frontiers in Microbiology. 2017;8.
15. Sadat Ebnerasool F, Motakef Kazemi N. Preparation and Characterization of Chitosan Nanocomposite Based on Nanoscale Silver and Nanomontmorillonite. Analytical Methods in Environmental Chemistry Journal. 2019;2(2):5-12.
16. Serrano E, Rus G, García-Martínez J. Nanotechnology for sustainable energy. Renewable and Sustainable Energy Reviews. 2009;13(9):2373-84.
17. Motakef Kazemi N, Salimi AA. Chitosan Nanoparticle for Loading and Release of Nitrogen, Potassium, and Phosphorus Nutrients. Iranian Journal of Science and Technology, Transactions A: Science. 2019;43(6):2781-6.
18. Abiodun Solanke IMF, Ajayi DM, Arigbede AO. Nanotechnology and its application in dentistry. Annals of Medical and Health Sciences Research. 2014;4(9):171.
19. Mehmandoust MR, Motakef-Kazemi N, Ashouri F. Nitrate Adsorption from Aqueous Solution by Metal–Organic Framework MOF-5. Iranian Journal of Science and Technology, Transactions A: Science. 2018;43(2):443-9.
20. Motakef Kazemi N. A novel sorbent based on metal–organic framework for mercury separation from human serum

samples by ultrasound assisted- ionic liquid-solid phase microextraction. Analytical Methods in Environmental Chemistry Journal. 2019:67-78.
21. González-Muñoz MJ, Rodríguez MA, Luque S, Álvarez JR. Recovery of heavy metals from metal industry waste waters by chemical precipitation and nanofiltration. Desalination. 2006;200(1-3):742-4.
22. Khedr MG. Nanofiltration and low energy reverse osmosis in rejection of radioactive isotopes and heavy metal cations from drinking water sources. DESALINATION AND WATER TREATMENT. 2009:342-50.
23. Wang S, Wu H. Environmental-benign utilisation of fly ash as low-cost adsorbents. Journal of Hazardous Materials. 2006;136(3):482-501.
24. Yang J, Hou B, Wang J, Tian B, Bi J, Wang N, et al. Nanomaterials for the Removal of Heavy Metals from Wastewater. Nanomaterials. 2019;9(3):424.
25. Alghamdi AA, Al-Odayni A-B, Saeed WS, Al-Kahtani A, Alharthi FA, Aouak T. Efficient Adsorption of Lead (II) from Aqueous Phase Solutions Using Polypyrrole-Based Activated Carbon. Materials. 2019;12(12):2020.
26. Sadati Behbahani N, Rostamizadeh K, Yaftian MR, Zamani A, Ahmadi H. Covalently modified magnetite nanoparticles with PEG: preparation and characterization as nano-adsorbent for removal of lead from wastewater. Journal of Environmental Health Science and Engineering. 2014;12(1).
27. Ricco R, Konstas K, Styles MJ, Richardson JJ, Babarao R, Suzuki K, et al. Lead(ii) uptake by aluminium based magnetic framework composites (MFCs) in water. Journal of Materials Chemistry A. 2015;3(39):19822-31.
28. Wang Y, Xie J, Wu Y, Ge H, Hu X. Preparation of a functionalized magnetic metal–organic framework sorbent for the extraction of lead prior to electrothermal atomic absorption spectrometer analysis. Journal of Materials Chemistry A. 2013;1(31):8782.
29. Shen J, Wang N, Wang Y, Yu D, Ouyang Xk. Efficient Adsorption of Pb(II) from Aqueous Solutions by Metal Organic Framework (Zn-BDC) Coated Magnetic Montmorillonite. Polymers. 2018;10(12):1383.
30. Musico YLF, Santos CM, Dalida MLP, Rodrigues DF. Improved removal of lead(ii) from water using a polymer-based graphene oxide nanocomposite. Journal of Materials Chemistry A. 2013;1(11):3789.
31. Ragab A, Ahmed I, Bader D. The Removal of Brilliant Green Dye from Aqueous Solution Using Nano Hydroxyapatite/ Chitosan Composite as a Sorbent. Molecules. 2019; 24(5): 847.
32. Wang Z, Sun K, He Y, Song P, Zhang D, Wang R. Preparation of hydroxyapatite-based porous materials for absorption of lead ions. Water Science and Technology. 2019;80(7):1266-75.
33. Irandoost M, Pezeshki-Modaress M, Javanbakht V. Removal of lead from aqueous solution with nanofibrous nanocomposite of polycaprolactone adsorbent modified by nanoclay and nanozeolite. Journal of Water Process Engineering. 2019;32:100981.
34. Seema KM, Mamba BB, Njuguna J, Bakhtizin RZ, Mishra AK. Removal of lead (II) from aqeouos waste using (CD-PCL-TiO2) bio-nanocomposites. International Journal of Biological Macromolecules. 2018;109:136-42.
35. Andrade FAC, Vercik LCdO, Monteiro FJ, Rigo ECdS. Preparation, characterization and antibacterial properties of silver nanoparticles–hydroxyapatite composites by a simple and eco-friendly method. Ceramics International. 2016;42(2):2271-80.
36. Mousa SM, Ammar NS, Ibrahim HA. Removal of lead ions using hydroxyapatite nano-material prepared from phosphogypsum waste. Journal of Saudi Chemical Society. 2016;20(3):357-65.
37. Kmiec E, Borjigin, Eskridge, Niamat, Strouse B, Bialk. Electrospun fiber membranes enable proliferation of genetically modified cells. International Journal of Nanomedicine. 2013:855.