Current Applied Science and Technology Vol. 20 No. 1 (January-April 2020)

Adsorbents Based on Keratin for Lead and Cadmium Removal

Viktoriia Havryliak[1*], Vasylyna Mykhaliuk[2], Romana Petrina[1], Olena Fedorova[1],
Vira Lubenets[1] and Volodymyr Novikov[1]

[1]Department of Technology of Biologically Active Substances, Pharmacy and Biotechnology,
Institute of Chemistry and Chemical Technology, Lviv Polytechnic National University, Lviv, Ukraine
[2] Laboratory of Animal Nutrition and Biosynthesis of Products,
Institute of Animal Biology NAAS, Lviv, Ukraine

Received: 15 October 2019, Revised: 27 December 2019, Accepted: 16 January 2020

Abstract

Keratins are an important source of biopolymers with high potential for application in various areas of biotechnology and biomedicine. Due to the presence of different functional groups in the structure of keratins, it can be used to bind the metal ions from aqueous solutions. Every year, tons of keratinous wastes are produced in the world especially in the wool textile industry. Therefore, the application of keratin biomaterial for the elimination of heavy metals from water is important for the environment. Our results have shown that the adsorption capacity of chemically modified keratin for Pb (II) and Cd (II) is higher than the untreated keratin and depends on pH. The highest adsorption efficiency for Pb (II) and Cd (II) was determined for sodium bisulfite-treated keratin at pH 6.0 (68.7 and 38.5% respectively). Under these conditions, Pb (II) and Cd (II) were much less adsorbed from solution by hydrogen peroxide-treated keratin (53.3 and 28.2% respectively). It is noteworthy that in the same model systems, the adsorption efficiency for Pb (II) is higher than for Cd (II). Our study showed that chemically treated keratin is a promising adsorbent for removing Pb (II) and Cd (II) ions from water solution, and would expand the application of keratin wastes.

Keywords: adsorption, cadmium, chemical treatment, keratin, lead
DOI 10.14456/cast.2020.3

1. Introduction

Anthropogenic pollution of the environment by heavy metals is becoming a priority threat to living organisms, including humans. Functioning chemical, metallurgical enterprises, and transport networks are the main factors that significantly increase the risk of heavy metal concentrations in ecosystems [1]. It is known that heavy metals can accumulate at all levels of the environmental pyramid and can be transmitted throughout the food chains. Their exposure leads to several adverse effect such as carcinogenesis, mutagenic impact, as well as toxic effect on the gastrointestinal tract, cardiovascular, endocrine, nervous, reproductive systems with the increasing risk of infertility [2].

---

*Corresponding author: Tel.: +38 050-431-6582
E-mail: vitahavryliak@gmail.com

Lead and cadmium are some of the biggest pollutants in the environment and their levels are constantly increasing. These heavy metals are generated into the environment mainly as a result of industrial activity and pose a serious threat to ecosystems. Thus, bioaccumulation of lead can cause impaired function of all systems in the body, especially renal, reproductive and nervous systems [3]. According to the information of the Institute for Health Metrics and Evaluation (USA) in 2017, lead exposure is the cause of 1.06 million deaths due to long-term effects on health, mainly in low- and middle-income countries [4].

Cadmium belongs to toxic ultramicroelements and its harmful effect on living organisms is manifested in very low concentrations. Bioaccumulation of cadmium in trophic chains leads to acute and chronic intoxication of living organisms, which can be accompanied by the impaired renal, central nervous system, immune system, psychological problems, etc [5]. Therefore, the urgent task is to search for an appropriate technique that can remove heavy metal ions from water with economical advantages.

There are various approaches for removing heavy metal ions from aqueous solutions such as chemical precipitation, ion exchange, reverse osmosis, filtration through semi-liquid membranes, adsorption [6]. However, their uses are often limited due to the high cost, energy costs, reagent requirements and incomplete removal of metal ions. Research data indicate that many substances of natural origin have sorbent properties [7-12]. From this point of view, biomaterials are considered as an alternative of new biosorbents when the price/efficiency ratio as well as the high adsorption capacity are taken into account. Thus, wool is characterized by the similar features. Significant advantages of keratin-based biosorbents are their availability, biodegradability, ability to regenerate [13-15].

Keratins differ from other structural proteins by the number of cysteine residues in the molecule (7-20% of the total amount). The presence of a large number of disulfide bonds is the basis for many chemical modifications of keratin that affect its physicochemical properties. Moreover, keratin contains a large number of ionized groups, in which the isoelectric point is 4-5 [16]. This characteristic provides the ability to bind heavy metals, cationic dyes, oil products from water, and some volatile substances. However, adsorption. of the pollutants by keratin depends on several factors, in particular, composition of the sorbent, surface area, pH of the solution, initial concentration of the pollutants, temperature, etc [16].

It is well known that keratin is able to remove contaminants through physisorption and chemisorption. Physisorption refers to the binding of metal ions on the surface or in the pores of keratin, whereas chemisorption is related to the ability of the main functional groups to form active chemical sites for the binding of metal ions. Natural keratin is highly ordered on the molecular level mainly due to its disulfide bonds which can limit the availability of reactive sites [13]. Therefore, variuos treatment can provide structural changes in the molecular organization of keratin. It is known that modification of wool fibers by chemical and physical agents can significantly increase its adsorption capacity [17-19].

The simplest methods of the chemical reorganization of keratin are oxidation and reduction. Hydrogen peroxide treatment of wool caused oxidation of disulfide bonds mainly to cysteic acid residues. The advantages of hydrogen peroxide application are its efficiency, low cost, and little toxicity. At the same time, bisulfite treatment provides the reconstruction of disulfide bonds with the formation of thiol and sulfonate residues. In the current study, the adsorption of Pb (II) and Cd (II) ions from aqueous solutions by keratin-based material was determined.

2. Materials and Methods

2.1 Materials

Raw wool was selected from a farm that belongs to the Institute of Animal Breeding in Steppe regions named by M. F. Ivanov, "Askania-Nova" (Ukraine). In experiments, the samples of low quality raw wool with a mean diameter of 30 µm were used. Wool fibers were washed with neutral detergent solution, rinsed many times with deionized water and dried at 22±1°C. Then lipids were removed from wool surface in the Soxhlet apparatus with carbon tetrachloride for 6 h.

2.2 Preparation of keratin-based biosorbent

For improving sorption capacity, wool was treated with 10% hydrogen peroxide and 0.2 M sodium bisulfite and placed into solutions at a ratio of 1:20 (w/V) for 3 h in a thermostat at 37°C. After treatment, the fibers were washed several times with deionized water and dried at room temperature. Then, chemically modified wool was ground and the resulting powder was used as a biosorbent for removal of heavy metals from their aqueous solutions. Chemically untreated keratin served as control

2.3 Experimental setup

Stock solutions of lead and cadmium ions were prepared by dissolving lead acetate and cadmium nitrate, respectively, in deionized water. Then, working metal solutions at 100 mg/l were obtained by dilution with DI water. The pH of the solutions was adjusted with 0.1 N HCl or 0.1 N NaOH and pH was varied between 5 and 7.

Keratin biosorbent (0.5 g) was placed in plastic flasks and 50 ml of the solution with a corresponding concentration of heavy metal was added. The flasks were shaken on a rotary shaker for one h and maintained for equilibrium for 24 h. The solutions were then filtered through filter paper and the concentration of Pb (II) and Cd (II) in the filtrates were determined by atomic absorption spectrophotometry.

2.4 Analytical methods

Biosorption efficiency was estimated by the equation [20]:

$$\% = \frac{C_i - C_e}{C_i} \cdot 100\%$$

where C_i and C_e are the initial and the final concentration of Pb (II) and Cd (II) ions in the aqueous solutions.

The adsorption capacity of keratin (mg/g) was calculated using the equation [20]:

$$q = \frac{q_0 - q_1 \cdot v}{m}$$

where

q_0 - the amount of metal ions in solution before adsorption;
q_1 - the amount of metal ions in solution after adsorption;
V - a volume of solution, L;
m - a mass of biosorbent, g.

For all experiments, analytical grade chemicals were used. The obtained data were analyzed by using ANOVA test. All results are expressed as means of five measurements ± standard error (x ± SE). For all statistical calculations, the significance was considered as the value of $P < 0.05$.

3. Results and Discussion

3.1 Pb (II) removal by keratin-based adsorbents

Keratinous biomaterials were used as a sorbent for the removal of lead from aqueous solutions. The adsorption capacity of Pb (II) by keratin-based biosorbent was studied in the pH range from 5.0 to 7.0. The higher adsorption capacity for these ions was observed for chemically treated keratin in our model systems (Figure 1). Keratin treated with sodium bisulfite was characterized by the highest adsorption of Pb (II) ions from aqueous solution in all experimental series. After the treatment of keratin with hydrogen peroxide, their adsorption capacity of Pb (II) ions increased compared to the untreated keratin, but was lower than for keratin treated with sodium bisulfite.

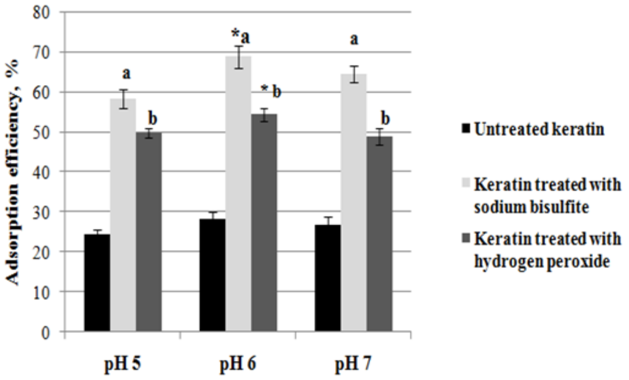

Figure 1. Adsorption efficiency of Pb (II) by keratin-based biosorbent

* - statistically significant differences between chemically treated keratin at pH 5 and pH 6;
a - statistically significant differences between untreated keratin and keratin treated with sodium bisulfite at pH 5 – pH 7;
b - statistically significant differences between untreated keratin and keratin treated with hydrogen peroxide at pH 5 – pH 7

When pH value was increased to 6.0, the adsorption efficiency of keratin-based sorbents also increased. It is noteworthy that under these conditions the adsorption efficiency of functionalized keratin was higher on 10.5 % for bisulfite treated keratin and on 5 % for keratin treated with hydrogen peroxide ($P<0.05$) compared with those at pH 5.0. However, it was reported that about 88% of Pb (II) was eliminated by precipitation with a keratin solution at pH 5 and the maximum absorption of Pb(II) was 43.3 mg/g and the removal of heavy metal ions also depends on the initial concentrations in solution [21]. Our results have shown that the adsorption efficiency of untreated keratin for Pb (II) ions practically did not exceed 30%. The chemical treatment of keratin was accompanied by a significant increase in the efficiency of the removal of Pb (II) ions from their solutions. These results indicate the increase of available functional groups on the keratin surface after treatment [22]. The better sorption properties of bisulfite-modified keratin can be explained by the formation of new thiol and sulfonate groups [23]. Some researchers believe that among different functional groups, the sulfur atoms can more readily coordinate to the heavy metal ions [24]. At the same time the lower sorption capacity of hydrogen peroxide treated keratin is obvious because of the products of cystine oxidation in the form of cysteic acid, cystine monoxide, cystine dioxide form less reactive groups [22]

Zhang *et al*. [22] have shown that chemical modification of human hair enhanced biosorption of heavy metals from solution due to the increase of surface area and the forming of new metal-binding site in the surface of keratin. According to the experimental data, the highest adsorption efficiency for Pb (II) was found for sodium bisulfite treated keratin at pH 6.0 whereas keratin treated with 10% hydrogen peroxide was slightly less bound to the Pb (II) ions. However, these results were significantly higher than untreated keratin. Similar results were observed in the study of adsorption of Pb (II) at pH 5.0 and 7.0. The data revealed that there were no significant differencies between the adsorption efficiency of chemically treated keratin-based biosorbent at pH 6.0 and 7.0. Our data showed that pH is significantly influenced the adsorption processes. It is known that there is the competition of H^+ ion adsorption with metal ions, therefore, the adsorption capacity at low pH is relatively small [25]. Our findings are consistent with the finding of Mahdavian [14] that the optimum pH at 5.8 is effective for biosorption of lead by human hair.

3.2 Cd (II) removal by keratin-based adsorbents

As can be seen in Figure 2, the adsorption capacity of Cd (II) ions by untreated keratin is quite low. After the chemical treatment with sodium bisulfite and hydrogen peroxide, the adsorption capacity of the biosorbent increases, but it significantly depends on the pH of the solution. The sorption performance of novel wool powders was studied and the optimum pH for Cu (I) and Cd (II) ions was found to be in the range of 6.0-7.0 [26].

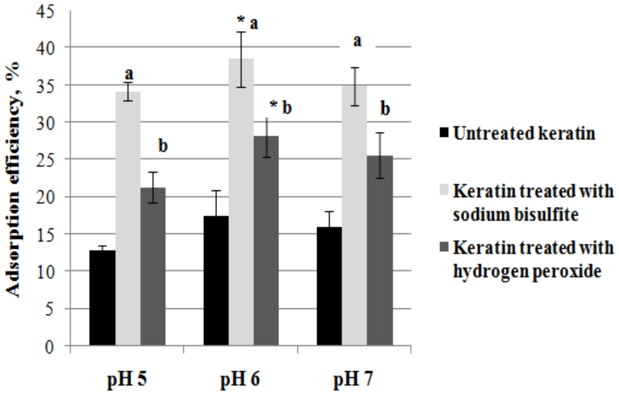

Figure 2. Adsorption efficiency of Cd (II) by keratin-based biosorbent

* - statistically significant differences between chemically treated keratin at pH 5 and pH 6;
a - statistically significant differences between untreated keratin and keratin treated with sodium bisulfite at pH 5 – pH 7;
b - statistically significant differences between untreated keratin and keratin treated with hydrogen peroxide at pH 5 – pH 7

Our study found that the adsorption efficiency of chemically-modified keratin increased at the pH 5.0 when compared with untreated keratin ($P<0.05$). With increasing pH to 6.0 the adsorption efficiency of keratin-based biosorbents increased. It is noteworthy that, as in the case of Pb (II), keratin treated with hydrogen peroxide binds Cd (II) ions less than keratin treated with sodium bisulfite. The lower adsorption efficiency of Cd (II) than Pb (II) can be explained that the size of ions influences the removal of metal ions from aqueous solution. With increasing atomic size of the metal, the adsorption becomes higher. In general, the outer shell of metals with a large atomic radius interacts more readily with proteins, including keratin [27]. It seems that with increasing pH to 6.0, the major functional groups on the keratin surface became deprotonated. As a result, the surface negative charge is increased, facilitating the binding of heavy metals [22].

According to the data presented in Figure 2, the adsorption capacity of chemically treated biosorbents did not differ at pH 5.0 and 7.0. But as in all previous results, the untreated keratin was characterized by significantly worse sorption properties compared to the modified ones. The similar results were observed for Cd (II) ions by using untreated human hair and other biofibers [22]. The adsorption efficiency of Cd (II) by untreated keratin-based biosorbent varied from 12.8 to 15..5% depending on the pH of the solution. At pH 6.0, the adsorption efficiency increased to 28.2% for keratin treated with hydrogen peroxide and 38.5% for keratin chemically modified by sodium bisulfite. Our results are in agreement with the finding that chemical treatment increases the affinity of keratin to heavy metal ions [22, 28]. Therefore, the maximum adsorption efficiencies for both Cd (II) and Pb (II) ions were observed for biosorbent based on keratin treated with sodium bisulfite. It is known that many functional groups (carboxyl, hydroxyl, amide, thiol/disulfide) were present in the structure of keratin [29]. It is obvious that the chemical treatment of keratin could lead to an increase in the functional groups on its surface. The thiol and sulfonate groups are formed as a result of the sulfitolysis enhancing the biosorption of heavy metals from solution [22].

In general, the affinity of keratin for lead ions was higher than for cadmium ions, which was due to stronger interactions between the functional groups with metal ions. On the other hand, the greater adsorption of Pb (II) can be related to its higher potential binding capacity and stability, especially of the Pb-S interation, and, perhaps, to the greater electrostatic interactions between Pb (II) and reactive sites of chemically treated keratin. According to the Hard and Soft Acid Base Principale such ions as Pb (II) form strong bond with CN^--, $R\text{-}S^-$, $\text{-}SH^-$, NH_2^-, which are groups containing sulfur and nitrogen atoms, whereas Cd (II) ions could form stable bonds mainly with SO_3^{2-}, O_2^- ligands [30]. Therefore, the differences in the adsorption capacity of Pb (II) and Cd (II) by the chemically modified keratin can be explained by the competition between protons and metal ions for specific binding sites on the surface of the keratin [22, 25].

4. Conclusions

The adsorption efficiency of heavy metals by keratin-based biosorbent depends on the pH of aqueous solutions. Maximum adsorption efficiency was observed at pH 6.0 for both Cd (II) and Pb (II) ions. Chemical treatment increased the adsorption capacity of keratin-based biosorbents. The best sorption properties for Cd (II) and Pb (II) have been found for keratin treated with sodium bisulfite. Under the same conditions in model systems, the adsorption efficiency of Pb (II) ions by keratin-based biosorbents was significantly higher than for Cd (II) ions due to the stronger interactions between Pb (II) ions and reactive sites of chemically treated keratin. The current study showed that increasing the adsorption capacity of biosorbents is possible by chemical modification of keratin and optimizing the corresponding parameters of the model systems.

References

[1] Ali, H., Khan, E. and Illahi, I., 2019. Environmental chemistry and ecotoxicology of hazardous heavy metals: Environmental persistence, toxicity, and bioaccumulation. *Journal of Chemistry*, 2019, Article ID 6730305, 1-14. https://doi.org/10.1155/2019/6730305.

[2] Masindi, V. and Muedi, K.L., 2018. *Environmental Contamination by Heavy Metals*. [e-book] London: IntechOpen. Available through: <https://www.intechopen.com/books/heavy-metals/environmental-contamination-by-heavy-metals>.

[3] Wani, A.L., Ara, A. and Usmani, J.A., 2015. Lead toxicity. *Interdisciplinary Toxicology*, 8 (2), 55-64.

[4] World Health Organization, 2019. *International Lead Poisoning Prevention Week of Action*. [online] Available at: https://www.who.int/ipcs/lead_campaign/en/

[5] Sharma, H., Rawal, N. and Mathew, B., 2015. The characteristics, toxicity and effects of cadmium. *International Journal of Nanotechnology and Nanoscience*, 3, 1-9.

[6] Song, J., Kong, H. and Jang, J., 2011. Adsorption of heavy metal ions from aqueous solution on by polyrhodanine-encapsulated magnetic nanoparticles. *Journal of Colloid and Interface Science*, 359 (2), 505-511.

[7] Ngwenya, S., Guyo, U., Zinyama, N.P., Chigondo, F., Nyamunda, B.C. and Muchanyereyi, N., 2019. Response surface methodology for optimization of Cd (II) adsorption from wastewaters by fabricated tartaric acid-maize tassel magnetic hybrid sorbent. *Biointerface Research in Applied Chemistry*, 9 (4), 3996-4005.

[8] Fadillah, G., Putri, E.N.K., Febrianastuti, S., Maylinda, E.V. and Purnawan, C., 2018. Adsorption of Fe Ions from Aqueous Solution Using α-Keratin-Coated Alginate Biosorbent. *International Journal of Environmental Science and Development*, 9 (3), 82-85.

[9] El-Gendy, M.M.A.A., Hassanein, N.M., Abd El-Hay, I.H.A. and Abd El-Baky, D.H., 2017. Heavy Metals Biosorption from Aqueous Solution by Endophytic *Drechslera hawaiiensis* of *Morus alba* L. derived from Heavy Metals Habitats. *Mycobiology*, 45 (2), 73-83.

[10] Poonam, Bharti, S.K. and Kumar, N., 2018. Kinetic study of lead ($Pb^{2+)}$ removal from battery manufacturing wastewater using bagasse biochar as biosorbent. *Applied Water Science*, 8, 119. https://doi.org/10.1007/s13201-018-0765-z

[11] Mondal, N.K. and Basu, S., 2019. Potentiality of waste human hair towards removal of chromium (VI) from solution: kinetic and equilibrium studies. *Applied Water Science*, 9, 49. https://doi.org/10.1007/s13201-019-0929-5

[12] Nodoushan, M.H., Ehrampoush, M.H., Rafati, L., Farzi, M. and Barzegar, K., 2015. Study of Co (II) adsorption from aqueous solution using protein granules produced from chicken feather. *Environmental Health Engineering and Management Journal*, 2 (4), 193-197.

[13] Ghosh, A. and Collie, S.R., 2014. Keratinous materials as novel absorbent systems for toxic pollutants. *Defence Science Journal*, 64 (3), 209-221.

[14] Mahdavian, L., 2012. Effects of magnetic field, pH and retention time on the lead (Pb^{2+}) adsorption by modified human hair, goat hair and sheep wool. *African Journal of Microbiology Research*, 6 (1), 183-189.

[15] Mousavia, S.Z., Manteghiana, M., Shojaosadatib, S.A. and Pahlavazadeha, H., 2018. Keratin nanoparticles: synthesis and application for Cu (II) removal. *Advances in Environmental Technology*, 2, 83-93.

[16] Shavandi, A, Silva, T.H, Bekhit, A.A. and Bekhit, A.E., 2017. Keratin: dissolution, extraction and biomedical application. *Biomaterials Sciences*, 5(9), 1699-1735.

[17] Hanzlikova, S., Branisa, J., Hybler, P., Sprinclova, I., Jomova, K. and Porubska, M., 2016. Sorption properties of sheep wool irradiated by accelerated electron beam. *Chemical Papers*, 70 (9), 1299-1308.

[18] Aluigi, A., Tonetti, C., Vineis, C., Varesano, A., Tonin, C. and Casasola, R., 2012. Study on the adsorption of Chromium (VI) by hydrolyzed keratin/polyamide 6 blend nanofibres. *Journal of Nanosciece and Nanotechnology*, 12(9), 7250-7259.

[19] Aluigi, A., Corbellini, A., Rombaldoni, F. and Mazzuchetti, G., 2012. Wool-derived keratin nanofiber membranes for dynamic adsorption of heavy-metal ions from aqueous solutions. *Textile Research Journal*, 83(15), 1574-1586.

[20] Khosa, M. A. and Ullah, A., 2014. In-situ modification, regeneration, and application of keratin biopolymer for arsenic removal. *Journal of Hazardous Materials*, 78, 360-371.

[21] Sekimoto, Y., Okiharu, T., Nakajima, H., Fudjii, T., Shirai, K. and Moriwaki, H., 2013. Removal of Pb (II) from water using keratin colloidal solution obtained from wool. *Environmental Sciences and Pollution Research,* 20 (9), 6531-6538.

[22] Zhang, H., Carillo, F., Lopes-Mesas, M. and Palet, C., 2019. Valorization of keratin biofibers for removing heavy metals from aqueous solutions. *Textile Research Journal,* 89 (7), 1153-1165.

[23] Sinkiewicz, I., Sliwinska, A., Staroszczyk, H. and Kołodziejska, I., 2017. Alternative methods of preparation of soluble keratin from chicken feathers. *Waste Biomass Valorization*, 8, 1043-1048.

[24] Dabrowski, A., Hubicki, Z., Podkoscielny, P. and Robens, E., 2004. Selective removal of the heavy metal ions from waters and industrial wasterwaters by ion-exchange method. *Chemosphere*, 56 (2), 91-106.

[25] Homagai, P.L., Paudyal, H. and Ghimire, K. N., 2008. Adsorption kinetics of Pb(II), Cd(II), Zn(II) and Fe(III) onto saponified apple waste. *Journal of Nepal Chemical Society*, 23, 102-105.

[26] Naik, R., Wen, G., Ms, D., Hureau, S., Uedono, A., Wang, X., Liu, X., Cookson, P.G. and Smith, S.V., 2010. Metal ion binding properties of novel wool powders. *Journal of Applied Polymer Science*, 115 (3), 1642-1650.

[27] Kar, P. and Misra, M., 2004. Use of keratin fiber for the separation of heavy metal from water. *Journal of Chemical Technology and Biotechnology*, 79 (11), 1313-1319.

[28] Khosa, M. A., Wu, J., and Ullah, A., 2013. Chemical modification, characterization, and application of chicken feathers as novel biosorbents. *RSC Advances*, 3, 20800-20810.

[29] Zahn, H., Wortmann, F. J., Wortmann, G., Schaefer, K., Hoffmann, R. and Finch, R., 2003. Wool. In: *Ullmann's Encyclopedia of Industrial Chemistry*. Vol. 39. 6th ed. Weinheim, Germany: Wiley-VCH Verlag, pp. 525-555.

[30] Wang, J. and Chen, C., 2009. Biosorbents for heavy metals removal and their future. *Biotechnology Advances*, 27 (2), 195-226.