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Utilization of Tannin-Based Biomaterials in the Removal of Boron from Aqueous Solution

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Abstract

In this study, valex, which has natural tannins, was produced from Turkish acorns (valonia) by spray drying method. Then, valex was used for adsorption studies of boron from aqueous solutions. Produced valex was also characterized by FTIR and SEM analysis. The results showed that boron could be removed from an aqueous solution by a tannin-based biosorbent. During the experimental part of this study, the effect of parameters such as pH, initial boron concentration, and adsorbent dosage on boron removal was observed. In addition, adsorption kinetics and adsorption isotherm studies were made. Maximum boron removal was obtained by the yield of 92.9 % at pH 3, initial boron concentration 8 ppm, and adsorbent dosage 1 g. The batch experiment best fit to Temkin isotherm and pseudo-second-order kinetic model.

Keywords: *Boron; spray drying; tannin; adsorption; bioadsorbent*

1. Introduction

Boron and its compounds are mainly used in agriculture, ceramics, glass, metallurgy, pharmaceuticals, textile, and paper industries. Among these industries, half of the boron production is used for glass industries. Also, ^{10}B isotope can keep the reaction rate under control to prevent a nuclear explosion in the nuclear industry [1]. Today, with the rapid increase of industrialization, the unconscious consumption of water resources has increased rapidly. The increase in consumption causes a rapid increase in the rate of waste in the water. Boron, one of these waste elements, threatens the life of all living things together with the increase in the proportion of the water [2]. Boron may be detrimental to both plants and animals above certain levels [3]. World Health Organization (WHO) revised the guideline value of boron to 2.4 mg/L [4]. In recent years, various separation methods such as adsorption, reverse osmosis [5], ion exchange [6], electrocoagulation [7], chemical precipitation [8], hybrid process [9] have been used to remove boron from aqueous solutions. Adsorption is a very promising method in aqueous solutions containing very low concentrations of boron [10]. Several sorbents are used in the adsorption process to remove boron from solution, including fly ash, clays, activated carbon, oxides, layered double hydroxides, nanoparticles, natural minerals, mesoporous silica, selective resins, biological materials, and complexing membranes [1].

Recently, bioadsorbents mostly have been utilized in the adsorbent process for water purification. Tannins are naturally occurring phenolic compounds, which have been a subject of extensive research leading to the development of a wide range of industrial applications. Tannins are high molecular weight polycyclic aromatic compounds widely distributed through the plants. Tannins are water-soluble compounds, so to use tannins as adsorbents; they need to be modified to insoluble tannin gels [5,11].

Tannins can be found in many plants. Oak, chestnut, pine, acacia, birch tree, beech, pomegranate is among the richest plants. Tannins can be found in the different parts of each plant, including crust, wood, fruit, and leaves. Acorn is a hard oval toothed fruit. It is called valonia in the form of chestnut. Valex, which is a commercial name of acorn's extract, contains a very rich tannin and is widely used in many fields; mainly in leather, pharmaceutics, and painting [12,13].

Spray dryers are essential units for conventional production processes, and they are used in many industries including food, pharmaceutical, chemical, ceramic, so on. Spray dryer is a chamber in which the liquid solution is sprayed by atomizer as droplets into hot flow gas, resulting in drying the liquid droplets. The atomization produces very small droplets that are able to efficiently evaporate the water in the very short residence time in the drying chamber. Regarding its obtainability and low cost, air is commonly preferred as hot gas stream after various heating processes. After drying, the particles are homogeneous and uniform and therefore have an effective surface area [14,15].

In this study, tannin-based bio adsorbent was produced with a spray dryer. This adsorbent was used boron removal study and, the effect of adsorption parameters such as pH, initial boron concentration and adsorbent dosage on boron removal were investigated. In addition, isotherm and kinetic model have been researched according to different models.

2. Materials and Methods

In this study, the valex was produced via spray drying from the acorns obtained from Artu Chemical Company. The adsorbent which is then to be used in the adsorption experiment of the valex was prepared. The produced adsorbent was added to the boron solution of the specific concentration and left to stir at 175 rpm in the shaken water bath for 24 hours. At last, the solution was analyzed by ICP analysis to determine the concentration after adsorption and the adsorption yield for the boron removal of the produced adsorbent was calculated.

2.1. Valex production from Turkish corns (valonia) via spray drying

The production of valex in classical method, firstly acorns were broken and then the grain sizes were reduced to 2 – 0.85 mm. Grinded acorns pellets taken in a beaker were added to 1/3 of water and stirred at 90°C for 8 hours. The solid phase was removed, and water and fresh oak pellets were added. In this way, the enrichment was carried out by the addition of gradually ground solid and water. The enriched liquid phase was further concentrated on a rotary evaporator, then centrifuged to remove impurities from the impurities. The pH of the resulting solution was measured as 3.3 and the density as 1.12 g/cm^3. At the last stage, the concentrated solution was fed to the spray drier (Yamato ADL310) at 180°C to complete the valex production.

2.2. Preparation of adsorbent

11.45 grams of valex was weighed and 50 mL of 13.3 N NH_3 solution was added and stirred. Then 37% formaldehyde solution was added. After mixing, the centrifuge was performed. After centrifugation, distilled water is added to the centrifuged precipitate and stirred in erlenmeyer. After mixing, the centrifuge was performed and 100 mL of 0.1 N nitric acid was added to the centrifuged precipitate. After the mixing process ends, the solution was centrifuged again. The adsorbent from the centrifuge was placed in a suitable glass container. The adsorbent was left in the oven for drying and aging. The adsorbent obtained after the drying process. Grain-reduced adsorbent was passed through a 75 micron-sized steel sieve and the obtained fraction was used in the experiments.

2.3. Adsorption experiments

Adsorption experiments were carried out to find the best values of pH, initial boron concentration and adsorbent dosage. pH experiments were carried out between 2-8, initial boron concentration experiments were carried out in 2, 4, 8, 12, 18 mg/L, adsorbent dosage experiments were carried out in 0.4, 0.6, 0.8, 1.2 g. The parameters were tested to obtain the best efficiency in the adsorption experiments. Equations (1) and (2) were used to find the concentration of the surface of solid and adsorption efficiency. Where m indicates the mass of adsorbent (kg), V is Volume (m^3), C_o the initial concentration, C_e the equilibrium concentration, q_e equilibrium adsorption capacity.

$$q_e = \frac{(C_o - C_e)}{m} \times V \quad (1)$$

$$Adsorption\ efficiency = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

3. Results and Discussion

3.1. Extraction experiment results

In the extraction study, the yield of valex production from the acorns was calculated to be 14%. The photograph of the commercial valex-1, commercial valex-2 and the valex produced from the Turkish acorns by the conventional method after extraction and spray dryer is shown in the Figure 1.

Figure 1. Produced valex (a), commercial valex-1 (b), commercial valex-2 (c)

3.2. Results of adsorption experiments

3.2.1. Effect of pH

In pH experiments, pH was changed between 2-8. Adsorption efficiency (%) and q_e values were found for pH values indicated in Table 1.

Table 1. Effect of pH on adsorption

pH	Equilibrium concentration, C_e (mg/L)	Adsorption capacity, q_e (mg/g)	Adsorption efficiency (%)
2	2.17	0.29	73.1
3	0.58	0.37	92.9
4	0.79	0.36	90.2
5	1.09	0.35	86.5
6	1.74	0.32	78.4
7	2.83	0.26	64.8
8	3.71	0.22	54.0

The best pH value in the experiment was found to be 3.

3.2.2. Effect of initial boron concentration

After selecting the best pH value as 3, the pH was kept constant at 3 for each initial concentration value. Besides, the amount of adsorbent was taken as 1 g. As shown in Table 2, adsorption efficiency values were found for the indicated initial concentrations.

Table 2. Effect of initial concentration on adsorption

Boron concentration (mg/L)	Equilibrium concentration, C_e (mg/L)	Adsorption capacity, q_e (mg/g)	Adsorption efficiency (%)
2	0.29	0.09	85.5
4	0.40	0.18	89.9
8	0.58	0.37	92.9
12	1.45	0.53	87.9
18	2.98	0.75	83.4

The best boron concentration in the experiment was found to be 8 ppm.

3.2.3. Effect of adsorbent dosage

The highest adsorption percentages were 3 in the pH parameter and 8 mg/L at the initial boron concentration. As shown in Table 3, adsorption yield values were found for the adsorbent dosage indicated.

Table 3. Effect of adsorbent amount on adsorption

Adsorbent dosage (g)	Equilibrium concentration, C_e (mg/L)	Adsorption capacity, q_e (mg/g)	Adsorption efficiency (%)
0.4	1.98	0.77	75.6
0.6	1.22	0.57	85.0
0.8	0.85	0.45	89.5
1.0	0.58	0.37	92.9
2.0	0.43	0.19	94.7

Although the highest adsorption efficiency was obtained in the dosage of 2 g adsorbent, 1 g adsorbent was used as the best parameter in the experiments.

3.2.4. Investigation of adsorption isotherms

During the last decade, three fundamental approaches formulated a wide variety of isotherm models such as Langmuir, Freundlich, Dubinin-Radushkevich, Temkin, Toth and various more isotherms. First approach considers the kinetics where the adsorption and desorption rates are equal, and the adsorption equilibrium will be defined as a state of dynamic equilibrium. The second approach is based on the thermodynamics, providing a framework deriving various adsorption isotherm models with different forms. Moreover, the main idea of generating the characteristic curve is conveyed by the third approach [16]. In Table 4, R^2 values of Langmuir [17], Freundlich [17,18], D-R [2,19], Temkin [20,21] and BET [21] were calculated by the equations in articles. Adsorption was found to be best suited to Temkin isotherm.

Table 4. Isotherm models

Isotherm Models	R^2
Langmuir	0.882
Freundlich	0.899
D-R	0.873
Temkin	0.978
BET	0.765

3.2.5. Investigation of adsorption kinetics

The principle of adsorption process is mainly divided into two stages: diffusion and surface reaction. Correspondingly, the adsorption kinetics model is also composed of two types: diffusion model and reaction model. The diffusion model focuses on the transport of adsorbates from the bulk solution to the adsorbent surface, such as the film-pore diffusion model and the homogenous surface diffusion model. [22]. The kinetic models used in this study are given in Table 5 and, R^2 values of pseudo-first order [23], pseudo-second order [23], Elovich [24] are listed.

Table 5. Kinetic models

Kinetic models	R^2
Pseudo-first-order kinetic model	0.935
Pseudo-second-order kinetic model	0.999
Elovich	0.994
First-order kinetic model	0.893
Second-order kinetic model	0.948
Intraparticle diffusion	0.936

Also, equations of first order [25], second order [23] and intraparticle diffusion [23] were calculated by the equations in articles. The pseudo-second-order kinetic model whose R^2 value is closest to the number 1 was chosen from the kinetic models we studied.

3.3. Results of FTIR analysis

After the valex was obtained, FTIR analysis was carried out to examine the general bond structure and to compare it with the commercial valex-1 and commercial valex-2 examples. The results of the analysis are shown in Figure 2.

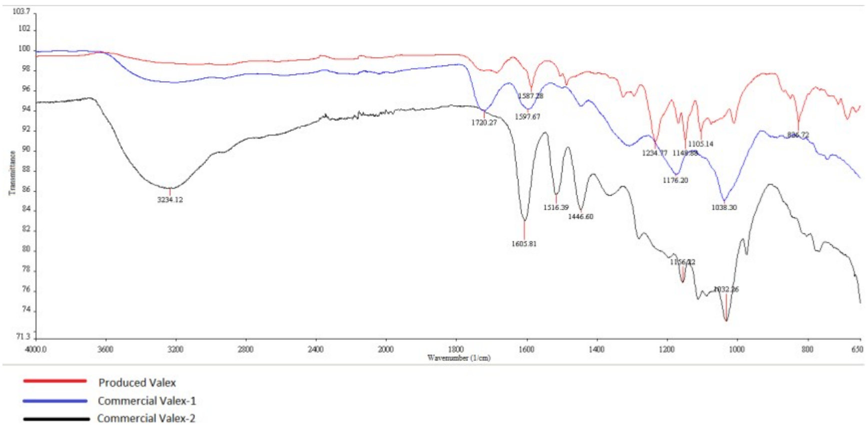

Fig. 2. FTIR analysis

The peaks formed in the spectrum obtained by FTIR were investigated in four regions. The first region has a wavelength between 4000 and 2500 cm-1, between 2500 and 2000 cm-1 in the second region, between 2000 and 1500 cm-1 in the third region, and between 1500 and 400 cm-1 in the fourth region, or fingerprint region [26]. The commercial valex-1 and commercial valex-2 valex did not peak in the first and second regions. This region is due to peak O-H bonds at 3234 cm-1 in the spectrum of commercial-2 valex [26]. In the third region, there is a peak at 1720 cm-1 for commercial valex-2. This peak is due to the C = O bond in the tannic acid structure of the valex. The peaks seen in the range of about 1600-1400 cm-1 wavelength in the three valex are caused by the aromatic C = C bonds, whereas the peaks seen between 1200 and 1000 cm-1 are due to the C=O bonds. In the fourth zone, called the fingerprint region, there was a pike with a wavelength of 826 cm-1 for the produced valex, but commercial valex-2 was not found. The peaks formed in this region are mostly due to the characteristic bonds. Because of the three valex do not have the same characteristics, it is unlikely that the peaks in this area will be identical in this region.

3.4. SEM results

Figure 3 illustrates the SEM micrographs of the valex samples obtained from the Turkish oak acorn. It can be seen from the figure that the most uniform spherical shape was found for the valex samples produced by the spray drying method. According to these SEM results, most of the granules were solid particles, the particle distribution was not uniform, and it had a high surface area. This is shown as an essential parameter that positively affects adsorption efficiency.

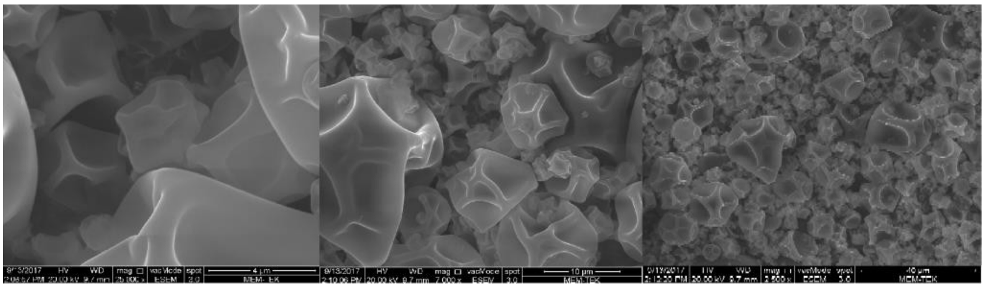

Fig. 3. SEM micrographs of the valex samples obtained from the Turkish acorns

4. Conclusion

The yield of valex production was found to be in the range of 10-15% in the literature. It was found to be 13.86% in this study. This is an acceptable value. To increase the yield, the extraction stage can be increased, and the extract phase concentration can be increased by the advanced enrichment method. Furthermore, after extraction, the concentration of the solution will increase the efficiency of feeding the spray dryer. It has been seen that the adsorbent produced from valex has a good result with 93% efficiency in boron removal [27]. The pH value of the solution is an essential parameter for the amount of boron adsorbed since it affects the ionization of boric acid. This study determined the pH value as 5.3 after the adsorbent solution was added to boric acid solution. According to optimum conditions, the pH value was adjusted to 3 by nitric acid solution, and the solution was adsorbed. The experiment can be repeated at different pH values to increase adsorption efficiency. However, higher pH should not be preferred as they may cause degradation of the grain structure [28]. The highest yield obtained under the most suitable conditions of pH 3, 8 ppm initial concentration, 1 g adsorbent, 25 ºC, and 24 hours was determined as 92.9%. Adsorption was best suited to the Temkin isotherm and pseudo-second-order kinetic model.

5. References

[1] Guan, Z.; Lv, J.; Bai, P.; Guo, X. Boron removal from aqueous solutions by adsorption—A review. Desalination 2016, 383, 29-37.

[2] Çalık, A. Bor mining and properties of Turkey. Engineer and Machine Journal 2002, 508, 1-9.

[3] Hilal, N.; Kim, G.J.; Somerfield, C. Boron removal from saline water: a comprehensive review. Desalination 2011, 273(1), 23-35.

[4] WHO Guidelines for Drinking-Water Quality, 4nd ed., World Health Organization, 2011.

[5] Wolska, J.; Bryjak, M. Methods for boron removal from aqueous solutions – A review. Desalination 2013, 310, 18-24.

[6] Mel'nik, L.A.; Butnik, I.A.; Goncharuk, V.V. Sorption-membrane removal of boron compounds from natural and wastewaters: Ecological and economic aspects. J.Water Chem.Technology 2008, 30, 167-169.

[7] Sarı, M.A.; Chellam, S. Mechanisms of boron removal from hydraulic fracturing wastewater by aluminum electrocoagulation. J.Colloid Interface Sci 2015, 458, 103-111.

[8] Yoshikawa, E.; Sasaki A.; Endo M. Removal of boron from wastewater by the hydroxyapatite formation reaction using acceleration effect of ammonia. Journal of Hazardous Materials 2012, 237-238, 277-282.

[9] Samatya, S.; Köseoğlu, P.; Kabay, N.; Tuncel, A.; Yüksel, M. Utilization of geothermal water as irrigation water after boron removal by monodisperse nanoporous polymers containing NMDG in sorption-ultrafiltration hybrid process. Desalination 2015, 364, 62-67.
[10] Xu Y.; Jiang, J.-Q. Technologies for Boron removal. Industrial & Engineering Chemistry Research 2008, 47(1), 16-24.
[11] Bacelo, H.A.M.; Santos, S.C.R.; Botelho, C.M.S. Tannin-based biosorbents for environmental applications - a review. Chemical Engineerig Journal 2016, 303, 575-587.
[12] Dığrak, M.; İlçim, A.; Alma, M.H.; Şen, S. Antimicrobial activites of the extracts of various plants. Turkish J.Biology, Tübitak 1999, 23, 241-248.
[13] Özacar, M.; Şengil, İ.A. The use of tannin from Turkish acorns (valonia) in water treatment as a coagulant and coagulant air. Turkish J. Eng.Env.Sci., Tübitak, 2002, 26, 255-263.
[14] Caglayan, H.; Şöhret, Y.; Caliskan, H. Thermo-ecologic evaluation of spray dryer for ceramic industry. Energy Procedia 2018, 144, 164-169.
[15] Tavan, Y.; Hosseini, S.H. A novel rate of the reaction between NaOH with CO_2 at low temperature in a spray dryer. Petroleum 2017, 3, 51-55.
[16] Al-Ghauti, M.A.; Da'ana, D.A. Guidelines for the use and interpretation of adsorption isotherm models: A review. Journal of Hazardous Materials 2020, 393, 122383.
[17] Chung, H.K.; Kim, W. H.; Park, J.; Cho, J.; Jeong, T. Y.; Park, P.K. Application of Langmuir and Freundlich isotherms to predict adsorbate removal efficiency or required amount of adsorbent. Journal of Industrial and Engineering Chemistry 2015, 28, 241-246.
[18] Ruan, G.; Yan, F.; Zhang, F.; Bhandari, N.; Ruan, G.; Dai, Z.; Zhang, K. Determination of adsorption isotherm parameters with correlated errors by measurement error models. Chemical Engineering Journal 2015, 281 921-930.
[19] Demirtaş, A. Boron and effects in plants. Atatürk University, Journal of Faculty of Agriculture 2005, 36(2), 217-225.
[20] Dada, A.; Olalekan, O.; Olatunya, A.; DADA, O. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherms Studies of Equilibrium Sorption of Zn 2+ Unto Phosphoric Acid Modified Rice Husk. IOSR Journal of Applied Chemistry 2012, 3(1), 38-45.
[21] Foo, K.; Hameed, B. Insights into the modeling of adsorption isotherm systems. Chemical Engineering Journal 2010, 156(1), 2-10.
[22] Fang, D.; Zhuang, X.; Huang, L.; Zhang, Q.; Shen, Q., Jiang, L. Developing the new kinetics model based on the adsorption process: From fitting to the comparison and prediction. Science of the Total Environment 2020, 725, 138490.
[23] Qiu, H.; Lv, L.; Pan, B.; Zhang, Q.; Zhang, W. Critical review in adsorption kinetic models. Journal Of Zhejiang University-Science A 2009, 10(5), 716-724.
[24] Juang, R.; Tseng, R.; Wu, F. Characteristics of Elovich equation used for the analysis of adsorption kinetics in dye-chitosan systems. Chemical Engineering Journal 2009, 150(2-3), 366-373.
[25] Arun, K.; Venkobachar, C. Removal of cadmium (II) by lowcost adsorbans, Journal of Environmental Engineering 1984, 110, 110–122. 104
[26] Özacar, M.; Şengil, İ.A. The use of tannin from Turkish acorns (valonia) in water treatment as a coagulant and coagulant air. Turkish J. Eng.Env.Sci., Tübitak 2002, 26, 255-263.
[27] Bacelo, H.A.M.; Santos, C.R.; Botelho, C.M.S. Tannin-based biosorbents for environmental applications - A review. Chemical Engineering Journal 2016, 303, 575-587.
[28] Erdem, P.; Bursali, E.; Yurdakoç, M. Preparation and characterization of tannic acid resin: study of boron adsorption. Dokuz Eylul University, Graduate School of Natural and Applied Sciences, İzmir, 2012.