Removal of chromium (Cr6+) from aqueous solutions using adsorption onto pistachio shell

Ruhollah Akbarpour (BSc) [1], Akram Ghorbanian (MSc) [2], Maryam Dolatabadi (MSc) [3,4*]

[1] *BSc in Environmental Health.*

[2] *Department of Environmental Health, School of Health, Mashhad University of Medical Sciences, Mashhad, Iran.*

[3] *Environmental Science and Technology Research Center, Department of Environmental Health Engineering, School of Public Health, Shahid Sadoughi University of Medical Sciences, Yazd, Iran.*

[4] *Student Research Committee, Kerman University of Medical Sciences, Kerman, Iran.*

Information

Article Type:
Original Article

Article History:

Received: 18.10.2021
Accepted: 18.12.2021

Doi: 10.22123/PHJ.2021.315737.1113

Keywords:
Hard pistachio shell
Hexavalent chromium (Cr^{6+})
adsorption
aqueous solutions

Corresponding Author:
Maryam Dolatabadi

Email: *Health.dolatabadi@gmail.com*

Tel: +98-9131695314

Abstract

Introduction: Among the environmental pollutants which have involved many parts of the world, one can observe the pollution caused by heavy metals such as hexavalent chromium (Cr^{6+}) , the presence of which in water causes many problems such as dysfunction of the skin, kidneys and liver as well as cancer. Thus, its removal from aqueous environments seems necessary. The present study has been conducted to investigate the efficiency of hard pistachio shell as a natural and inexpensive adsorbent for the removal of Cr^{6+} from aqueous solutions.

Materials and Methods: The study was performed experimentally and on a laboratory scale, and it was attempted to investigate the effect of effective parameters such as reaction time, solution pH, adsorbent amount (hard pistachio shell) and Cr^{6+} concentration on removal efficiency. Kinetic studies and adsorption isotherms were also investigated.

Results: The results showed that the maximum removal of Cr^{6+} was 98.2% under optimal conditions including reaction time of 60 minutes, pH of 9, adsorbent amount of 2 g/L and Cr^{6+} concentration of 10 mg/L. Kinetic studies showed greater agreement with second order kinetics (R^2= 0.9929). Also, the Cr^{6+} adsorption process followed Langmuir adsorption isotherm (R^2= 0.9965).

Conclusion: According to the obtained results, it can be concluded that hard pistachio shell can be used as a cheap and suitable and also environmentally friendly adsorbent to remove Cr^{6+} from aquatic solutions.

►Please cite this article as follows:
Akbarpour R, Ghorbanian A, Dolatabadi M. Removal of chromium (Cr6+) from aqueous solutions using adsorption onto pistachio shell. Pistachio and Health Journal. 2021; 4 (4): 80-90.

1. Introduction

Access to safe and clean water is essential for maintaining human health and the development of communities. The growth of urbanization and industrialization has led to a sharp increase in the volume of wastewater. Environmental destruction due to the disposal of polluted wastewater from sources of production is a serious problem in various countries, which is more critical in developing countries due to the fact that wastewater is discharged without being treated or is inefficiently treated. Water pollution is mainly due to the rapidly declining source of this vital substance and is one of the most serious challenges in the 21st century [1, 2]. The presence of various pollutants in water sources can be a serious threat to human health. Heavy metals are among the most dangerous and growing pollutants, and among heavy metals, chromium is of special importance for its high toxicity in very small amounts [3, 4]. Based on epidemiological studies, the relationship between chromium and cancer has been confirmed, including the investigation of this element in lung, stomach, prostate and central nervous system cancers [5, 6].

The absorption of this metal in organisms depends on its capacity, so that the absorption of Cr^{6+} in drinking water is 9 times higher than the absorption of Cr^{3+} [7, 8]. Complications of being exposed to Cr^{6+} include skin irritation and skin ulcers, respiratory tract irritation, and liver and kidney disorders. Cr^{6+} at 10 mg/kg body weight also causes liver necrosis, nephritis, and gastrointestinal and lung cancer (9, 10). WHO has also confirmed the carcinogenicity of Cr^{6+} in humans and has set the recommended maximum for Cr^{6+} in drinking water to be 0.01 mg/L. To prevent increased Cr concentrations in water resources, the United States EPA has set the acceptable level of Cr^{6+} of wastewater in surface water to be 0.01 mg/L. Also, in order to maintain and improve the level of public health in the community, this agency has set an acceptable level in drinking water to be 0.05 mg/L. The maximum allowed amount of Cr^{6+} in drinking water according to the Standard 1053 of the Iranian Institute of Standards and Industrial Research is 0.05 mg/L [11-13].

So far, various processes have been used to remove Cr^{6+}, including electrochemical, ozonation, coagulation and sedimentation processes, and membrane processes, including reverse osmosis, as well as adsorption processes, each of which has certain advantages and disadvantages [14-16]. As for biological processes, heavy metals in high concentrations have a toxic effect on the microorganisms involved in the purification process and reduce the efficiency of the system. Membrane processes, despite their considerable efficiency, have high operating and utilizing costs, and they are not very, thus, welcomed in developing countries. Among all technologies, the adsorption method is less important due to its environmental friendliness, economical, high removal efficiency, ease of operation and management, and the ability to the production of an adsorbent that produces less sludge. Various adsorbents such as powdered and granular activated carbon, carbon nanotubes and alumina, etc. have been used for this purpose [17, 18]. Meanwhile, activated carbon is used in many refining processes due to its adsorption capacity and high efficiency, but its production and regeneration costs are expensive. Some waste products from industrial and agricultural operations, and natural materials and bio-absorbents are potentially cost-effective alternatives. Agricultural products are economical absorbents because they are abundant in environment, and are effective sorbents [19, 20]. Agricultural wastes include: maize wood, sugarcane pulp, sugarcane kernels, rice hulls and pistachio shells, coal, sawdust, charcoal, bituminous coal, straw and agricultural waste are cheaper and more renewable sources of additional activated carbon. These wastes have little or no economic value and there is often a problem with their disposal [21, 22].

In a study using pistachio shells, Yetilmezsoy et al removed lead from aqueous solutions. Under optimal conditions including pH of 5.5, adsorbent amount of 1 g, initial lead concentration of 30 mg/L, and temperature of 30 °C, the lead removal percentage was 93% (23). Aghajani et al have used soft pistachio shells as agricultural by-products to remove lead (II) and mercury (II) from aqueous and wastewater solutions. Their results have indicated that the maximum removal of lead was 90.9% at pH 6, the reaction time of 80 minutes, at a temperature of 25 °C, and the maximum removal of mercury was 91.5% at pH 6 and a temperature of 25°C for 100 minutes [24]. Therefore, special attention should be given to these low-cost products. Iran, with 440,000 hectares of area under cultivation of pistachio, currently accounts for about 57% of world production of this product and is known as the largest and most important pistachio-producing country. Consequently, one of the by-products of pistachio is hard shell of pistachio that should be disposed of after being consumed. Therefore, one of the problems we are facing is the disposal and management of pistachio waste. Thus, this study attempts to investigate using hard shell of pistachio as an adsorbent to remove Cr^{6+}.

2. Materials and methods

This study, hard pistachio shells were collected from Kerman city. The shells were then crushed in a mill, washed with distilled water and dried. To remove possible pollutants, the resulting material was washed in 2% hydrochloric acid and then rinsed with distilled water to remove acid residue, and then dried at 80 °C for 4 hours. After being dried, using the standard sieves (with a mesh size of 60-100 µm) meshing was conducted, and it was then used as an adsorbent to remove Cr^{6+}. Then, it was attempted to investigate the effect of various parameters including reaction time, solution pH, the amount of adsorbent (hard pistachio shell) and the concentration of Cr^{6+}. A certain amount of adsorbent (hard pistachio shell) was in contact with the amount of chromium in certain concentrations at different pHs. After the reaction time, the samples were collected and analyzed. Cr^{6+} removal percentage (R) and adsorbent adsorption capacity (q_e) were measured using Equations 1 and 2 [25].

$$\% R = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

In order to analyze and determine the control mechanism of adsorption processes such as adsorption on the surface, chemical reaction and adsorption of Cr^{6+} on hard pistachio shell, first and second order kinetic models were investigated. Also in this study, two isotherms were studied. The Langmuir model has uniform and limited adsorption sites for single-layer adsorption. The equation of Langmuir isotherm is equation 3 [25].

$$\frac{Ce}{qe} = \frac{1}{bqm} + \frac{Ce}{qm} \quad (3)$$

qe is the amount of Cr^{6+} adsorbed in the adsorbent mass in terms of mg/g and qm indicates the adsorption capacity, Ce is the equilibrium concentration of Cr^{6+} in solution after adsorption in terms of mg/L and b is Langmuir constant. In other words, the Freundlich equation expresses adsorption at a heterogeneous level in terms of adsorption energy and it is defined as Equation (4) [25].

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \quad (4)$$

In which Ce is the equilibrium concentration of Cr^{6+} in solution after adsorption in terms of mg/L, qe is the adsorption capacity at equilibrium (mg/g), and Kf andn are Freundlich constants. The experimental data were evaluated by Microsoft Excel to determine the removal percentage and investigate isotherms and kinetics.

3. Results

Effect of reaction time

In order to determine the appropriate time, the sampling adsorption process was investigated at 10 to 90 minutes at constant conditions (pH equal of 7.5, Cr^{6+} concentration 5 mg/L, and adsorbent amount of 1.5 mg/L). As Figure 1 indicates, the removal percentage increases with increasing reaction time. Elimination efficiencies at 10, 20, 30, 45, 60, and 90 minutes were reported to be 13.1%, 31.4%, 56.8%, 74.3%, 78.8%, and 79.3%, respectively. As shown in Figure 1, with increasing the contact time from 10 to 60 minutes, the removal percentage increases rapidly, but with increasing the reaction time to 90 minutes, the increase in efficiency has been confirmed with a relatively small slope; minute 60 has been thus introduced as the optimal time.

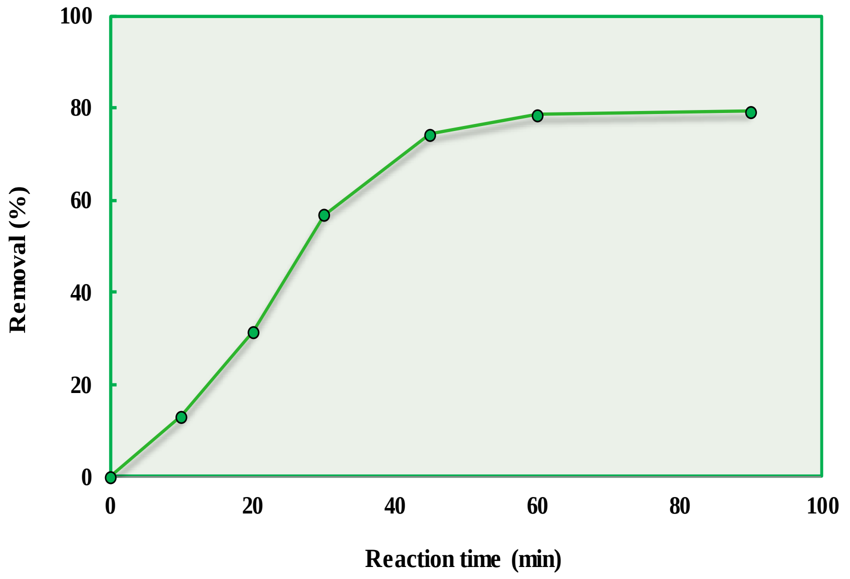

Figure 1. Effect of reaction time on Cr^{6+} removal efficiency.

The effect of solution pH

pH is effective parameters in the adsorption process. In this study, it was attempted to investigate the effect of soluble pH on Cr^{6+} removal in the range of 4 to 11 under constant conditions including Cr^{6+} concentration of 5 mg/L, adsorbent amount of 1.5 g/L and reaction time of 60 minutes. As shown in Figure 2, with increasing pH, the removal efficiency increases significantly; by increasing pH from 4 to 11, the efficiency increased from 38.3% to 94.6%. Moreover, at the pH of 9 and 11, there was not much difference in removal efficiency (less than 3%), so in the experiments, pH was considered to be 9.

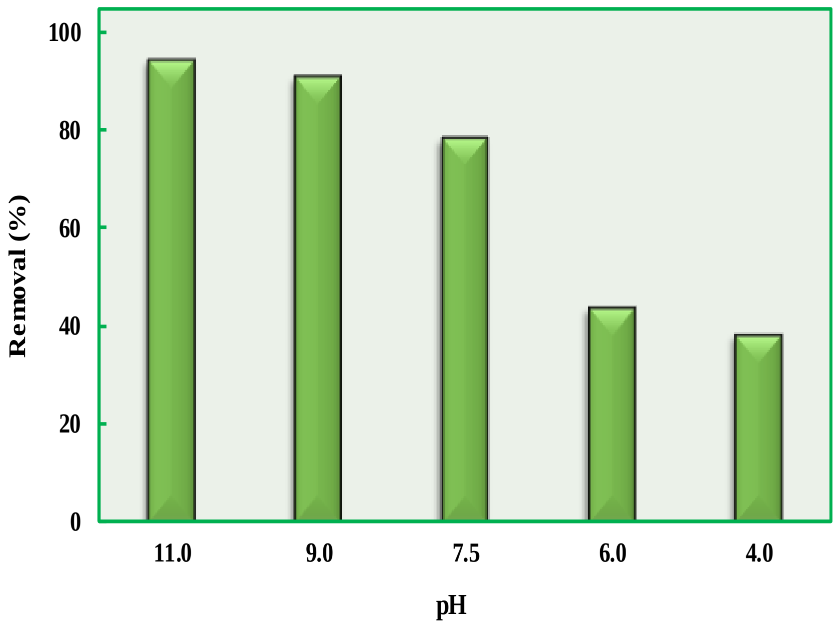

Figure 2. Effect of pH on Cr^{6+} removal efficiency.

The effect of adsorbent amount (hard pistachio shell)

In this study, it was attempted to investigate the effect of the amount of adsorbent in the range of 0.5 to 2.5 grams per liter. To evaluate the amount of adsorbent, all experiments were conducted at pH 9, the concentration of Cr^{6+} was 5 mg/L, and reaction time was 60 minutes. According to Figure 3, when the amount of adsorbent increases, the removal percentage increases as well; in the adsorbent amounts of 0.5, 1, 1.5, 2 and 2.5, the removal percentage of Cr^{6+} is 63.4%, 80.6%, 91.1%, 100% and 100%, respectively. Due to the optimal percentage of the amount of adsorbent in amounts 2 and 2.5 g/L on the removal of Cr^{6+}, in other stages of research, the amount of adsorbent was considered to be 2 g/L.

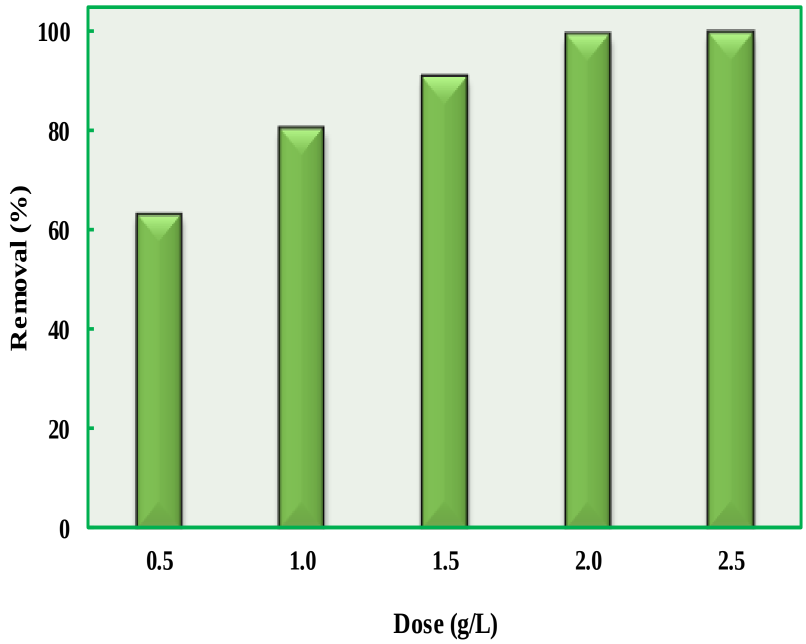

Figure 3. Effect of adsorbent amount on Cr^{6+} removal efficiency.

Effect of Cr^{6+} concentration

The results of investigating the concentration of Cr^{6+} on the removal percentage at constant pH conditions of 9 and the adsorbent amount of 2 g/L and reaction time of 60 minutes are shown in Figure 4. As can be seen in the diagram, the removal percentage decreases with increasing concentration. Cr^{6+} removal efficiencies at concentrations of 5, 10, 15, 20 and 30 mg/L were reported to be 100%, 98.2%, 84.6%, 75.3% and 52.1%, respectively.

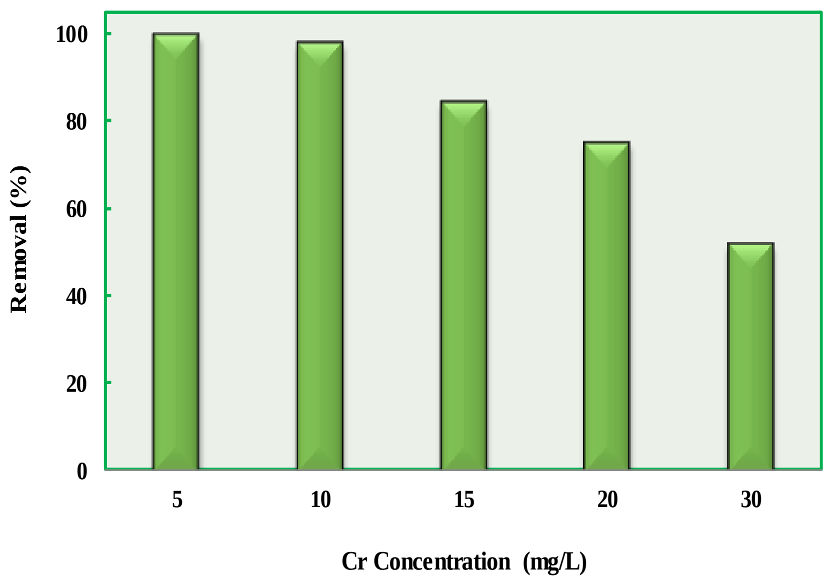

Figure 4. Effect of Cr^{6+} concentration on Cr^{6+} removal efficiency.

Adsorption kinetics and isotherms

First and second order kinetics and Freundlich and Langmuir adsorption isotherms were conducted under optimal conditions. The results are offered in Table 1.

Table 1. The constant parameters for the kinetic and isotherm adsorption.

Kinetic parameters						
First-order			Second-order			
K_1 (1/min)	qe (mg/g)	R^2	K_2 (g.min/mg)	q_e (mg/g)	R^2	
0.0074	43.7	0.9054	0.0093	32.2	0.9929	
Isotherm parameters						
Freundlich			Langmuir			
K_f (L/g)	n	R^2	q_m (mg/g)	b (L/mg)	R_L	R^2
13.4	3.2	0.9036	53.1	1.39	0.063	0.9965

4. Discussion

Reaction time is an integral part of any process, especially the adsorption process. In this study, contact time of 10 to 90 minutes were studied. The results have indicated that the adsorption process has an increasing trend for up to 60 minutes and after that, the adsorption process reaches equilibrium and shows a relatively stable trend. The effect of contact time can be expressed in this way that with increasing the contact time, the probability of Cr^{6+} ions colliding with the adsorbent increases and as a result, the removal percentage increases; in other words, the residual value decreases and the adsorption capacity increases (26, 27). pH is important factor in the absorption of pollutants. The pH of the reaction environment between the adsorbent and the adsorbed material is important factors influencing adsorption experiments. pH affects the adsorption efficiency by affecting the number of positive and negative charges on the adsorbent surface as well as changing the ionic state of metals and their ionization. The pH of the solution has a large effect on the adsorption of heavy metals due to the surface charge and the degree of ionization of the adsorbent. A study conducted by Bozic et al, which investigated the uptake of heavy metal ions by deciduous sawdust, has also indicated that the removal percentage of heavy metals increased with increasing pH (28). Due to the fact that the hard shell of pistachio has a pH_{pzc} of 5.2, at pHs lower than 2.5, it has a positive charge and at pHs above 2.5, the adsorbent has a negative charge. Also, Cr^{6+} has a positive and cationic charge. Therefore, at alkaline pHs, electrostatic attraction is established between the adsorbent (hard pistachio shell) and Cr^{6+}; this increases the removal percentage (29, 30).

Determining adsorbent mass is one of the topics that should be considered in adsorption studies. The results showed that with increasing the adsorbent mass from 0.5 to 2.5 g/L, the removal percentage increases as well. Increasing the amount of adsorbent leads to increased active surface points and increased number of active adsorption sites. With increasing the amount of adsorbent, due to high adsorption sites, the surface area increases. It can also be stated that at a constant concentration of pollutants, with increasing the amount of adsorbent, the ratio of active sites, high adsorbent molecules will be high; efficiency will, thus, increase. While in low adsorbent amounts the ratio of active sites to molecules of the adsorbent decreases, and, as a result, the adsorption decreases (31-33). The concentration of the pollutant. The results showed that with increasing the concentration, the removal percentage decreases. This is because the adsorbent has a limited number of active sites, so at high concentrations, the active sites adsorbed by the pollutant saturate more quickly, and this will reduce the process efficiency, as well as, increasing the concentration will encourage adsorption capacity (34-36).

5. Conclusion

In this study, Cr^{6+} removal was conducted using hard pistachio shell, and it was attempted to investigate the effect of important variables including reaction time, solution pH, adsorbent amount and Cr^{6+} concentration on removal efficiency. The maximum removal percentage under optimal conditions was 98.2%. The amount of adsorbent (hard pistachio shell), reaction time and pH of the solution were directly associated with removal efficiency, but the concentration of Cr^{6+} as a pollutant had a negative effect on the removal process and with increasing concentration, the removal percentage decreased. Moreover, kinetic and adsorption isotherm studies indicated more agreement with quadratic kinetics and Langmuir isotherm. According to the obtained results, it can be concluded that hard pistachio shell can be a suitable and cost-effective adsorbent for the removal of Cr^{6+} from aqueous solutions and even Cr^{6+} contaminated wastewater.

Acknowledgments

The authors would like to express their appreciation to the student research committee of Kerman University of Medical Sciences. The current work was conducted, after receiving approval from the ethics committee of [IR.KMU.REC.1395.438].

References

1- Tiadi N, Mohanty M, Mohanty C, H. Panda HP. Studies on adsorption behavior of an industrial waste for removal of chromium from aqueous solution. South African Journal of Chemical Engineering. **2017**;23(1):*132-8*.

2- Owalude SO, Tella AC. Removal of hexavalent chromium from aqueous solutions by adsorption on modified groundnut hull. Beni-suef university journal of basic and applied sciences. **2016**;5(4):*377-88*.

3- Pratush A, Kumar A, Hu Z. Adverse effect of heavy metals (As, Pb, Hg, and Cr) on health and their bioremediation strategies: a review. International Microbiology. **2018**;21(3):*97-106*.

4- Xia S, Song Z, Jeyakumar P, Shaheen SM, Rinklebe J, Ok YS, Bolan N, Wang H. A critical review on bioremediation technologies for Cr (VI)-contaminated soils and wastewater. Critical reviews in environmental science and technology. **2019**;49(12):*1027-78*.

5- Jobby R, Jha P, Yadav AK, Desai N. Biosorption and biotransformation of hexavalent chromium [Cr (VI)]: a comprehensive review. Chemosphere. **2018**;207:*255-66*.

6- Karimi-Maleh H, Ayati A, Ghanbari S, Orooji Y, Tanhaei B, Karimi F, Alizadeh M, Rouhi J, Fu L, Sillanpää M. Recent advances in removal techniques of Cr (VI) toxic ion from aqueous solution: a comprehensive review. Journal of molecular liquids. **2021**;329:*115062*.

7- Almeida JC, Cardoso CE, Tavares DS, Freitas R, Trindade T, Vale C, Pereira E. Chromium removal from contaminated waters using nanomaterials–a review. TrAC Trends in Analytical Chemistry. **2019**;118:*277-91*.

8- Mitra S, Sarkar A, Sen S. Removal of chromium from industrial effluents using nanotechnology: a review. Nanotechnology for Environmental Engineering. **2017**;2(1):*1-14*.

9- Aigbe UO, Osibote OA. A review of hexavalent chromium removal from aqueous solutions by sorption technique using nanomaterials. Journal of Environmental Chemical Engineering. **2020**:*104503*.

10- Othmani A, Magdouli S, Kumar PS, Kapoor A, Chellam PV, Gökkuş Ö. Agricultural waste materials for adsorptive removal of phenols, chromium (VI) and cadmium (II) from wastewater: A review. Environmental Research. **2021**:*111916*.

11- Levankumar L, Muthukumaran V, Gobinath M. Batch adsorption and kinetics of chromium (VI) removal from aqueous solutions by Ocimum americanum L. seed pods. Journal of hazardous materials. **2009**;161(2-3):*709-13*.

12- Ma J, Chen K. Designing porous nickel architectures for adsorptive removal of Cr (VI) to achieve drinking water standard. Separation and Purification Technology. **2020**;241:*116705*.

13- Nazir R, Khan M, Masab M, Rehman HU, Rauf NU, Shahab S, Ameer N, Sajed M, Ullah M, Rafeeq M. Accumulation of heavy metals (Ni, Cu, Cd, Cr, Pb, Zn, Fe) in the soil, water and plants and analysis of physico-chemical parameters of soil and water collected from Tanda Dam Kohat. Journal of pharmaceutical sciences and research. **2015**;7(3):*89*.

14- Fernández PM, Viñarta SC, Bernal AR, Cruz EL, Figueroa LI. Bioremediation strategies for chromium removal: current research, scale-up approach and future perspectives. Chemosphere. **2018**;208:*139-48*.

15- Karimi-Maleh H, Orooji Y, Ayati A, Qanbari S, Tanhaei B, Karimi F, Alizadeh M, Rouhi J, Fu L, Sillanpää M. Recent advances in removal techniques of Cr (VI) toxic ion from aqueous solution: a comprehensive review. Journal of molecular liquids. **2020**:*115062*.

16- Fallahzadeh RA, Eslami H. Electro-Oxidation as an Effective Technology in Removal of Persistent Organic Pollutants of Wastewater from Processing Pistachios. Pistachio and Health Journal. **2020**;3(3):*1-5*.

17- Tran HN, Nguyen DT, Le GT, Tomul F, Lima EC, Woo SH, Sarmah AK, Nguyen HQ, Nguyen PT, Nguyen DD. Adsorption mechanism of hexavalent chromium onto layered double hydroxides-based adsorbents: A systematic in-depth review. Journal of hazardous materials. **2019**;373:*258-70*.

18- Arora R. Adsorption of heavy metals–A review. Materials Today: Proceedings. **2019**;18:*4745-50*.

19- Lakherwal D. Adsorption of heavy metals: a review. International journal of environmental research and development. **2014**;4(1):*41-8*.

20- Ghorbanian A, Mahroudi A, Eslami H, Dolatabadi M. Removal of Methylene Blue Dye from Textile Industry Wastewater by Sawdust of Pistachio Tree. Pistachio and Health Journal. **2020**;3(4):*63-76*.

21- Inyang MI, Gao B, Yao Y, Xue Y, Zimmerman A, Mosa A, Pullammanappallil P, Ok YS, Cao X. A review of biochar as a low-cost adsorbent for aqueous heavy metal removal. Critical Reviews in Environmental Science and Technology. **2016**;46(4):*406-33*.

22- Fallahzadeh RA, Tahmasebimoradi M, Soltani Gerdefaramarzi N, Torabidost P, Eslami H. A Review of Strategies for Using Pistachio Waste. Pistachio and Health Journal. **2021**;4(1):*86-95*.

23- Yetilmezsoy K, Demirel S. Artificial neural network (ANN) approach for modeling of Pb (II) adsorption from aqueous solution by Antep pistachio (Pistacia Vera L.) shells. Journal of hazardous materials. **2008**;153(3):*1288-300*.

24- Aghajani Z, Zand-Monfraed M, Bahmani-Androod S. Removal of lead (II) and mercury (II) from aqueous solutions and waste water using pistachio soft shell as agricultural by-products. Fresenius Environ Bulletin. **2014**;5:*170-6*.

25- Najafpoor AA, Soleimani G, Ehrampoush MH, Ghaneian MT, Salmani ER, Dolatabadi Takabi M. Study on the adsorption isotherms of chromium (VI) by means of carbon nano tubes from aqueous solutions. Environmental Health Engineering and Management Journal. **2014**;1(1):*1-5*.

26- Rashid R, Shafiq I, Akhter P, Iqbal MJ, Hussain M. A state-of-the-art review on wastewater treatment techniques: the effectiveness of adsorption method. Environmental Science and Pollution Research. **2021**;12:*1-17*.

27- Kulbir S, Abdullahi WS, Chhotu R. Removal of heavy metals by adsorption using agricultural based residue: A review. Res J Chem Environ. **2018**;22(5):*65-74*.

28- Božić D, Gorgievski M, Stanković V, Štrbac N, Šerbula S, Petrović N. Adsorption of heavy metal ions by beech sawdust–Kinetics, mechanism and equilibrium of the process. Ecological Engineering. **2013**;58:*202-6*.

29- Arain MB, Ali I, Yilmaz E, Soylak M. Nanomaterial's based chromium speciation in environmental samples: a review. TrAC Trends in Analytical Chemistry. **2018**;103:*44-55*.

30- Valentín-Reyes J, García-Reyes R, García-González A, Soto-Regalado E, Cerino-Córdova F. Adsorption mechanisms of hexavalent chromium from aqueous solutions on modified activated carbons. Journal of environmental management. **2019**;236:*815-22*.

31- Liu W, Yang L, Xu S, Chen Y, Liu B, Li Z, Jiang C. Efficient removal of hexavalent chromium from water by an adsorption–reduction mechanism with sandwiched nanocomposites. RSC advances. **2018**;8(27):*15087-93*.

32- Kausar A, Iqbal M, Javed A, Aftab K, Bhatti HN, Nouren S. Dyes adsorption using clay and modified clay: a review. Journal of Molecular Liquids. **2018**;256:*395-407*.

33- Lima EC, Hosseini-Bandegharaei A, Moreno-Piraján JC, Anastopoulos I. A critical review of the estimation of the thermodynamic parameters on adsorption equilibria. Wrong use of equilibrium constant in the Van't Hoof equation for calculation of thermodynamic parameters of adsorption. Journal of molecular liquids. **2019**;273:*425-34*.

34- Gupta SS, Bhattacharyya KG. Kinetics of adsorption of metal ions on inorganic materials: a review.

Advances in colloid and interface science. **2011**;162(1-2):*39-58*.

35- Uddin MK. A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade. Chemical Engineering Journal. **2017**;308:*438-62*.

36- Adeyemo AA, Adeoye IO, Bello OS. Adsorption of dyes using different types of clay: a review. Applied Water Science. **2017**;7(2):*543-68*.