

NATURAL AKSIL AS ADSORBENT FOR REMOVAL OF HEXAVALENT CHROMIUM FROM WATER RESOURCES: EQUILIBRIUM AND KINETICS

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Abstract

One of the most important problems today is the pollution of water resources with heavy metals, especially pollution with hexavalent chromium. The removal of Cr(VI) from wastewater is important due to its toxicity to living organisms and the environment. For this reason, in this paper we have focused on the removal of Cr(VI) ions using a natural mineral adsorbent such as aksil (Kriva Palanka). Adsorption experiments were conducted at room temperature, at different initial concentrations of Cr(VI) ions and different amounts of adsorbent. The results obtained from this work have been used to model the balance of the adsorption process, through several adsorption isotherms, using the MATLAB software package. For the equilibrium analysis of the adsorption system Cr(VI) with aksil, the following adsorption isotherms were applied: Langmuir, Freundlich, Langmuir-Freundlich and Redlich-Peterson. In order to define the kinetics of the investigated Cr(VI)-aksil system, these models have been applied: I and II order, pseudo I and pseudo II order and model of Elovic.

Keywords: hexavalent chromium, aksil, wastewater, adsorption, kinetics.

Introduction

Environmentally responsible wastewater disposal requires a reduction in the concentration of Cr(VI), up to its complete elimination. In this direction, numerous techniques have been developed for the removal of hexavalent chromium from wastewater, such as: adsorption, Advanced Oxidation Processes (AOPs), nanofiltration (NF), reverse osmosis (RO), ion exchange with resins and the use of membrane systems. The negative sides of these techniques are incomplete removal, high energy requirements, generation of toxic waste and large capital and investments (Babel *et al.*, 2007). In recent years, adsorption has emerged as an alternative method for the removal of metal ions from wastewater, including Cr(VI). To reduce capital costs, extensive research has been conducted into the use of cheaper adsorbents, which can be various types of earths and clays (Gupta *et al.*, 2001). Various minerals have been used such as: carbonized eggshells (Berihu *et al.*, 2026), walnut-derived biosorbents (Rajni *et al.*, 2023), activated carbon (Wang *et al.*, 2023), eucalyptus tereticornis bark (Sharma *et al.*, 2011), powdered leaves of *Prosopis cineraria* (Soleimani *et al.*, 2024), unmodified and modified biomass (Tripathi *et al.*, 2024), green algae (Valli *et al.*, 2013). The use of materials in solid form to remove certain substances from gases and liquid solutions is a process known as adsorption and in essence this process involves the distribution of substances from gas or liquid phase on the surface of a solid substrate, this process is most widely used for separation and purification purposes. In this process, the substances used for adsorption, in this case, change the concentration of heavy metals. An adsorbent is a solid body on which adsorption takes place, while the adsorbate is the substance that is adsorbed. In terms of the molecular layers that are created during adsorption, we have polymolecular adsorption. The division into physical and chemical adsorption is also known and they refer to the actions of the adsorbate molecules in relation to the surface of the adsorbent. In chemical adsorption, we have the formation of a chemical bond, while in physical adsorption, we have the appearance of the action of Van der Waals forces (Chamarthy *et al.*, 2001).

Materials and Methods

2.1 Adsorbent: To investigate the removal of hexavalent chromium from polluted waters in this work, we have used aksil (trade name/natural mineral complex). The adsorbent is mechanically prepared in a ball mill until granulation occurs, with the 0,25-0,5 mm fraction dominates. Aksil is a sedimentary complex sample with significant presence of amorphous SiO₂. The macroscopic image of the aksil is shown in Figure 1.



Figure 1. Aksil

The results of the scanning electron microscopy of the material-aksil show the presence of particles in various irregular shapes and dimensions in which there are no pores.

The morphological characteristics of the aksil with the Electronic Scanning Microscope are shown in Figure 2.

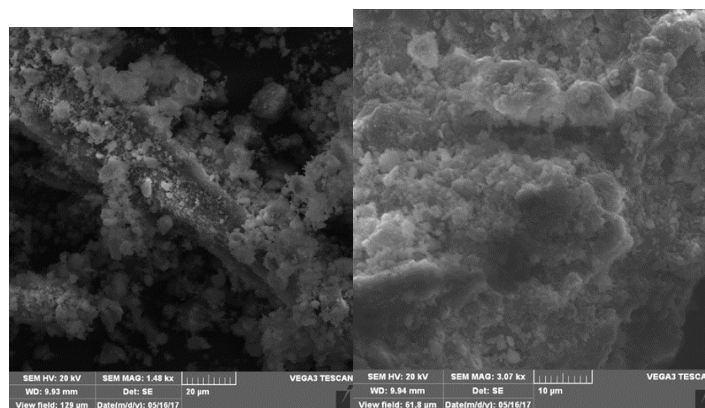


Figure 2. ESM of aksil

2.2 Adsorption experiment: A series of experiments were conducted in order to define the equilibrium and kinetics of the Cr(VI) ion separation process. The working mineral raw material that is the subject of the research of this paper was examined in a batch, laboratory reactor with a volume of 2,5 dm³, at room temperature, at a constant mixing mode of 500 rpm with a magnetic stirrer, during which the effect of the following operating parameters was monitored: pH of the medium (1, 2), initial concentration of Cr(VI) ions (0.3, 0.4, 0.5, and 0.6 mg/l), adsorption time (5, 10, 20, 30, 60, 90, 120 and 180 minutes), concentration of adsorbent (0.5; 1.5; 2.5; 3.5; 4.5; and 5.5 g/l). Aqueous solution of K₂Cr₂O₇ was used to prepare the standard solutions.

Results and Discussion

The decrease in the concentration of chromium ions, with the adsorption time, for different initial concentrations, is given in Figure 3,4. From the diagrams, a similar effect of contact time on the change in the concentration of Cr (VI) ions can be observed for used adsorbent. For all tested initial metal concentrations, rapid adsorption occurs in the first 30 min and maximum efficiency in the removal of Cr(VI) ions is achieved.

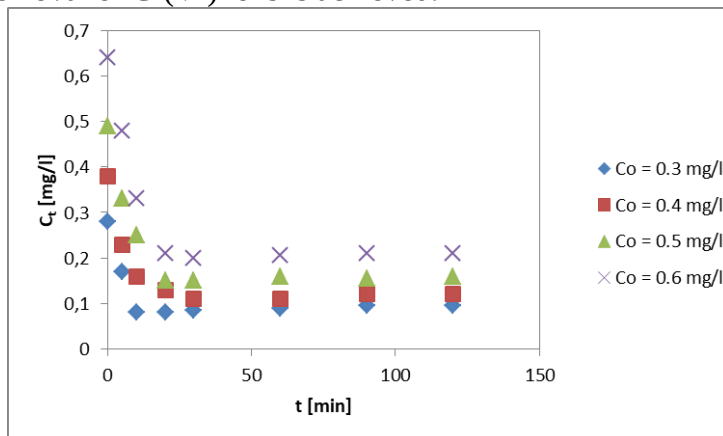


Figure 3. Dependence of Cr(VI) concentration from time of adsorption for the system Cr(VI)-aksil, pH=1

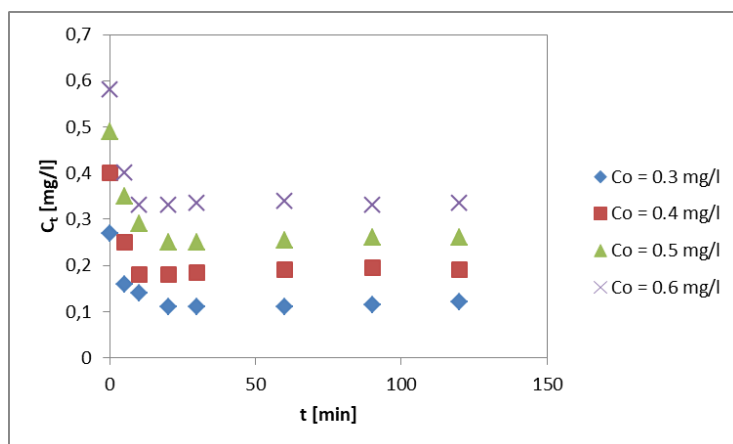


Figure 4. Dependence of Cr(VI) concentration from time of adsorption for the system Cr(VI)-aksil, pH=2

From the figures it can be seen that, adsorption equilibrium is reached in about 30 min. After this adsorption time, there is almost no change in the adsorbed amount of the tested adsorbate.

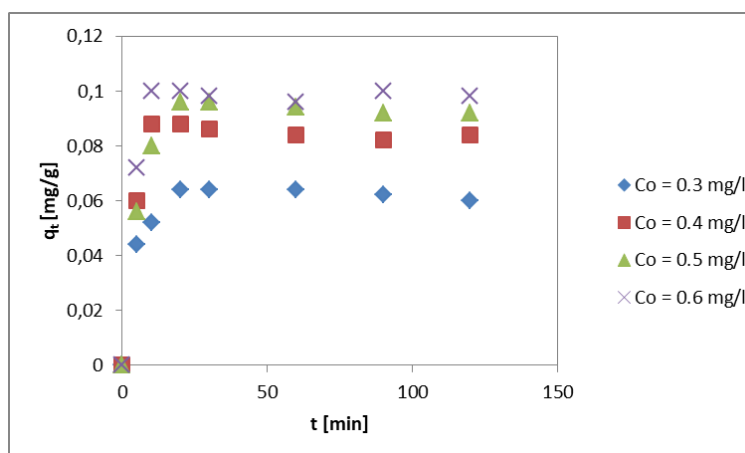


Figure 5. Dependence of adsorbed amount from time of adsorption for the system Cr(VI)-aksil pH=2

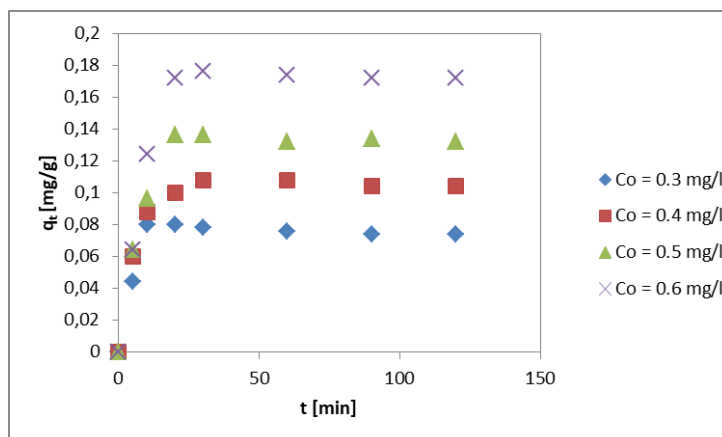


Figure 6. Dependence of adsorbed amount from time of adsorption for the system Cr(VI)-aksil pH=1

From the presented graphical dependences for the change in adsorption capacity with time, it is evident that at lower pH values, due to the phenomenon of protonation on the surface of the adsorbent, rapid adsorption occurs in the first 20-35 minutes.

Adsorption isotherms describe the equilibrium of the adsorbed material on the surface of the adsorbent. In this paper, the Langmuir, Freundlich, Langmuir-Freundlich and Redlich-Peterson isotherms are used in order to predict the adsorption behavior of Cr(VI) in aksil as an adsorbent. The diagram of the adsorption isotherms for the examined system is given in Figure 7. The fitting of the experimental results was performed using the MATLAB/Curve Fitting Toolbox software package. Table 1 presents the data resulting from the examination of the adsorption isotherms. The values of the model parameters are given as well as the values of the correlation coefficients, R^2 .

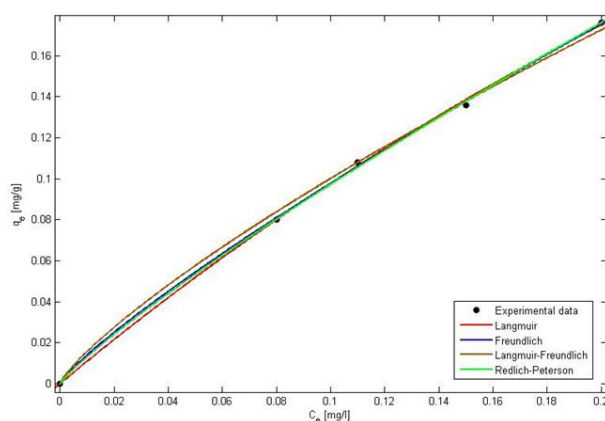


Figure 7. Adsorption isotherms for the adsorption of Cr(VI) with aksil

Table 1. Equilibrium isotherm parameters for the adsorption of Cr(VI) by aksil

Isotherm	Parameters and correlation coefficients	Aksil
Langmuir	q_m [mg/g]	0,1942
	K_L [l/mg]	21,34
	R^2	0,9972
Feundlich	K_F [l/g]	0,2571
	n	2,247
	R^2	0,9994
Langmuir-Freundlich	q_m [mg/g]	1,632
	K_C [l/mg]	0,1478
	n	1,72

Redlich-Peterson	R^2	0,9853
	K_{RP} [l/g]	92,408
	A [l/mg]	657
	β	0,458
	R^2	0,9985

The values of the parameters and correlation coefficients for the Cr(VI)-aksil system are given in Table 1. The correlation coefficient is the parameter according to which we select the isotherm that best matches the experimental results. From this Table we can conclude that the value of the correlation coefficient for the Freundlich isotherm is 0.9994. Accordingly, the Freundlich isotherm model is the better for fitting the experimental data compared to other isotherm models for the sorbent aksil.

The kinetics of Cr(VI) were analyzed using the following kinetic models: I and II order, pseudo I and pseudo II order and model of Elovic. The agreement between experimental and model values is expressed by the correlation coefficient R^2 . The largest value of R^2 for a kinetic model means that model successfully describes the kinetic adsorption of Cr(VI).

From Table 2, it can be seen that the correlation coefficient R^2 has the highest value for the given pseudo II order model, from here we can conclude that the kinetic adsorption of Cr(VI) by aksil can be described by the pseudo II order model.

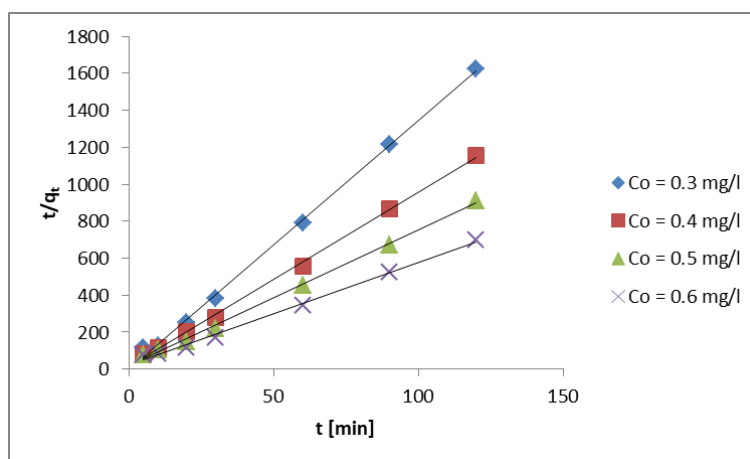


Figure 8. Pseudo II order kinetic model, Cr(VI)-aksil, pH=1

Table 2. Kinetic adsorption parameters, Cr(VI)-aksil, pH=1

Kinetic models	Parameters	A metal ion Cr(VI)			
	C_0 , екс. [mg/l]	0,3	0,4	0,5	0,6
	q_e , екс. [mg/g]	0,08	0,108	0,136	0,176
I - order	k_1 [min^{-1}]	0,0042	0,0062	0,0065	0,0068
	C_0 [mg/l]	0,1310	0,1997	0,2736	0,3727
	R^2	0,171	0,3825	0,3965	0,4242
II - order	k_2 [l/mg·min]	0,0261	0,0349	0,0268	0,0213
	C_0 [mg/l]	0,1149	0,1815	0,2472	0,3374
	R^2	0,122	0,4164	0,4021	0,4397

Pseudo I order	k_1 [min ⁻¹] q_e [mg/g] R^2	0,0169 0,0229 0,3317	0,0221 0,0379 0,6895	0,032 0,0697 0,821	0,0293 0,0518 0,5472
Pseudo II order	k_2 [g/mg·min] q_e [mg/g] R^2	7,2553 0,0744 0,9984	6,1857 0,1064 0,9985	2,7879 0,1367 0,9976	1,4510 0,1799 0,9955
Elovic	α [mg/g·min] β [mg/g] R^2	76,1573 178,57 0,265	1,0803 81,9672 0,6796	0,2826 51,0204 0,6692	0,1555 33,4448 0,6809

Research on the kinetics of the Cr(VI)-aksil system has also been done at pH=2, from which we can conclude that the correlation coefficient R^2 has a higher value in the given pseudo II order model, from here we can conclude that the kinetics of Cr(VI) adsorption with aksil at pH=2 can be described by the pseudo II order model. The results for the Cr(VI)-aksil system at pH=2 are given in Figure 9 and Table 3.

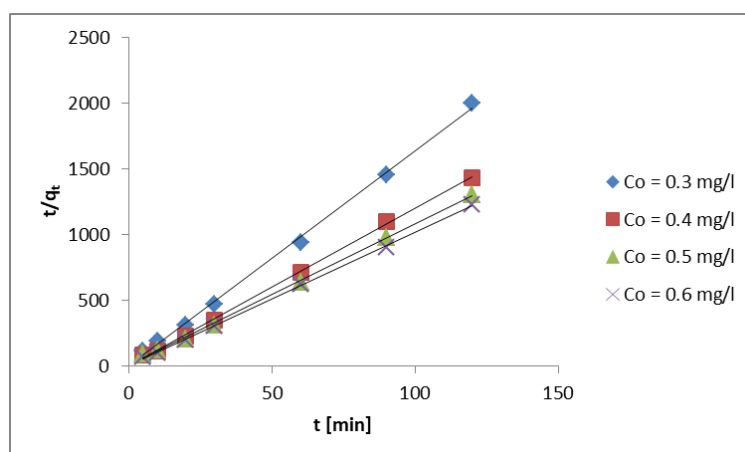


Figure 9. Pseudo II order kinetic model, Cr(VI)-aksil, pH=2

Table 3. Kinetic adsorption parameters, Cr(VI)-aksil, pH=2

Kinetic models	Parameters	A metal ion Cr(VI)			
	C_0 ,екс. [mg/l]	0,3	0,4	0,5	0,6
	q_e ,екс. [mg/g]	0,064	0,088	0,096	0,1
I - order	k_1 [min ⁻¹] C_0 [mg/l] R^2	0,0037 0,1579 0,2758	0,0027 0,2387 0,1884	0,003 0,3312 0,3007	0,0022 0,4001 0,2309
II - order	k_2 [l/mg·min] C_0 [mg/l] R^2	0,0233 0,1493 0,2861	0,0103 0,2270 0,1781	0,009 0,3205 0,3129	0,0052 0,3903 0,2409
Pseudo I order	k_1 [min ⁻¹] q_e [mg/g] R^2	0,0207 0,0265 0,7259	0,0187 0,0229 0,396	0,0244 0,0357 0,6592	0,0265 0,0266 0,5556

Pseudo II order	k_2 [g/mg·min] q_e [mg/g] R^2	0,2483 0,0613 0,998	0,2534 0,0835 0,9992	0,0120 0,0933 0,9988	0,0169 0,0990 0,9994
Elovic	α [mg/g·min] β [mg/g] R^2	0,0106 200 0,5637	$3,91 \cdot 10^4$ 238,095 0,2511	3,1988 106,38 0,5674	$7,96 \cdot 10^3$ 185,185 0,3799

Conclusions

This paper examines the removal of Cr(VI) from water resources using aksil. An aqueous solution of $K_2Cr_2O_7$ was used to prepare the working solutions. To determine the concentration before and after the Cr(VI) adsorption process, an atomic adsorption spectrophotometric method and UV/VIS Spectrophotometer were used. A series of experiments were conducted in order to define the equilibrium and kinetics of the Cr(VI) ion separation process. The working mineral raw material that is the subject of the research of this paper was examined in a batch, laboratory reactor with a volume of $2,5 \text{ dm}^3$, at room temperature, at a constant mixing mode of 500 rpm with a magnetic stirrer, during which the effect of the following operating parameters was monitored: pH of the medium (1,2), the initial concentration of Cr(VI) ions (0.3, 0.4, 0.5 and 0.6 mg/l), adsorption time (5,10,20,30,60,90,120 and 180 minutes), adsorbent concentration (0.5; 1.5; 2.5; 3.5; 4.5; and 5.5 g/l). To describe the adsorption equilibrium, we used the following adsorption isotherms: Langmuir, Freundlich, Langmuir- Freundlich and Redlich-Peterson using the MATLAB/Curve Fitting Toolbox software package. From the experimental values in this paper we can conclude that the value of the correlation coefficient for the Freundlich isotherm is 0.9994. Therefore, the Freundlich isotherm model is better for fitting the experimental data compared to other isotherm models for the sorbent aksil. From the kinetic adsorption parameters it can be seen that the correlation coefficient R^2 has the highest value for the given pseudo II order model, from here we can conclude that the kinetic adsorption of Cr(VI) with the working raw materials can be better described by the pseudo II order model.

References

- [1]. Babel S., and Opiso E.M., 2007. Removal of Cr from synthetic wastewater by sorption into volcanic ash soil. *International Journal of Environmental Science & Technology*, Vol. 4. No.1, pp.99-107.
- [2]. Gupta V.K., Gupta M., and Sharma S., 2001. Process development for the removal of lead and chromium from aqueous solutions using red mud-an aluminium industry waste. *Water research*, Vol. 5. No. 35, pp.1125-1134.
- [3]. Berihu G. G., Desbelom W. H., Mebrahtom G. W., Birhane E. T., and Maebele G. Z., 2026. Response surface optimization of hexavalent chromium removal from real tannery wastewater using carbonized eggshells. *Discover Sustainability*, Vol.7. No. 664.
- [4]. Rajni G., Rishav G., Mika S., Alimuddin M. A. K., Nabisab M. M., Yie H. T., 2023. Rapid adsorptive removal of chromium from wastewater using walnut-derived biosorbents. *Sci. Rep.* Vol. 1. No. 13, 6859
- [5]. Wang B., Lan J., Bo C., Gong B., Ou J., 2023 Adsorption of heavy metal onto biomass-derived activated carbon. *RSC Adv.*, Vol.7. No.13, pp.4275-4302.
- [6]. Sharma I., and Goyal D., 2011. Chromium removal from industrial effluent by *Eucalyptus tereticornis* bark. *Asian J. Exp. Sci.*, Vol.1. No. 25. pp. 29-35.
- [7]. Soleimani M., Jamali H. A., Mousazadehgavan M., Ghanbari R. (2024). Chromium adsorption using powdered leaves of *Prosopis cineraria*: kinetic, isotherm and optimization by response surface methodology. *Desalin. Water Treat.* 317, 100286. Wesner G.M., Ewing, J. J., Lineck, T.S., Jr., and Hinrichs, D.J. 1977. Energy conservation in municipal wastewater treatment.
- [8]. Tripathi M., Pathak S., Singh R., Singh P. K., Shukla A. K., (2024). A comprehensive review of lab-scale studies on removing hexavalent chromium from aqueous solutions by using unmodified and modified waste biomass as adsorbents. *Toxics*, Vol. 9. No.12, 657.

- [9]. Valli V. G., Rao G., Sridevi V., Keerthi K. (2013). Optimization of process parameters for biosorption of chromium using green algae. Parameters, Vol.6. No.2.
- [10]. Chamorthy S., Seo C. W. and Marshall W. E., (2001). Adsorption of selected toxic metals by modified peanut shells. Journal of Chemical Technology and Biotechnology, Vol.6. No. 76, pp. 593-597