# ADSORPTION OF HEXAVALENT CHROMIUM FROM AN AQUEOUS SOLUTION OF STEEL-MAKING SLAG

## ADSORPCIJA HEKSAVALENTNEGA KROMA IZ VODNE RAZTOPINE JEKLARSKE ŽLINDRE

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A batch removal of Cr(VI) ions from an aqueous solution under different experimental conditions using steel-making slag as a low-cost adsorbent is presented in this paper. The obtained results showed that the steel-making slag is an effective adsorbent for the removal of Cr(VI) ions from aqueous solutions. The adsorption of Cr(VI) with the steel-making slag follows the Langmuir isotherm equation. Among the tested kinetics models in this study (pseudo-first-order, pseudo-second-order, Elovich and intraparticle-diffusion models), the pseudo-second-order equation successfully predicted the adsorption. The thermodynamic parameters for the adsorption process were determined and discussed.

Keywords: adsorption, Cr(VI) ions, steel-making slag, isotherms, kinetic, thermodynamic

V članku je predstavljena raziskava odstranjevanja ionov Cr(VI) iz vodne raztopine z jeklarsko žlindro kot poceni adsorbenta pri različnih eksperimentalnih razmerah. Dobljeni rezultati so pokazali, da je jeklarska žlindra učinkovit adsorbent za odstranjevanje Cr(VI) ionov iz vodnih raztopin. Adsorpcija ionov Cr(VI) z jeklarsko žlindro se sklada z Langmuirovo izotermno enačbo. V tej študiji je od preizkušenih kinetičnih modelov (psevdo prvega reda, psevdo drugega reda, Elovichev model in model difuzije med delci) enačba psevdo drugega reda uspešno napovedala adsorpcijo. Določeni in obravnavani so termodinamični parametri za proces adsorpcije.

Ključne besede: adsorpcija, ioni Cr(VI), jeklarska žlindra, izoterme, kinetika, termodinamika

## 1 INTRODUCTION

Over the last few decades, due to their increased use in the treatment of metals and ceramic, glass production, mining operations and the production of batteries, various heavy metals were released into terrestrial and aquatic ecosystems.[1] The increase in the environmental contamination with heavy metals is a big concern for ecological systems and human health due to their toxicity, accumulation in food and persistence in nature.[2]

The main focus in water and wastewater treatment is given to hexavalent chromium due to its carcinogenic properties.[3] Cr(VI) ions are considered as one of the top 16 toxic pollutants and due to their carcinogenic effect on humans, they have become a serious health problem.[4] Cr(VI) ions can be released into the environment from various industrial operations such as the treatment of metals, production of iron and steel and the production of inorganic chemicals.[5]

Heavy metals can be removed from aqueous solutions using various techniques such as ion exchange,[6] precipitation[7] and adsorption.[8] Adsorption has been successfully used to remove heavy metals.[9] For several decades, activated carbon has been used as an adsorbent for the purification of industrial wastewater.[10] Although it is a most appropriate adsorbent for removing heavy metals, its widespread use was limited due to its high cost. Steel-making slag as an alternative adsorbent has been used to remove heavy metals in the environmental field. Due to its unique properties, steel-making slag is used as an alternative adsorbent for removing heavy metals from aqueous solutions. Steel-making slag is a by-product of the steel production and a waste material that is widely used due to its useful properties.[11]

## 2 EXPERIMENTAL WORK

Adsorption experiments were performed using the batch-equilibration technique. The initial concentrations of Cr(VI) ions were prepared in the range of 50–300 mg/L of dissolving $K_2Cr_2O_7$ in distilled water. A series of Erlenmeyer flasks containing steel-making-slag samples 1 g and solutions 50 mL were sealed until equilibrium was obtained. Then the adsorbent was removed by filtration. The concentration of Cr(VI) ions was determined using an atomic absorption spectrometer with a graphite furnace, equipped with Zeeman background correction. A Cr hollow-cathode lamp operating at the current of 4 mA was used as a line source. The measurements were performed at 357.9 nm, with the slit fixed at 0.8 nm. The atomization was carried out with the following parameters: $T = 2400$ °C, the ramp rate of 1200 °C/s and the dwell time of 6 s.[12] Each analysis was performed in triplicate and the average value was taken as the result. The chemical composition of the steel-making slag was determined with the standard chemical analysis[13] and the result in mass fractions ($w$) is: CaO – 36 %, MgO –
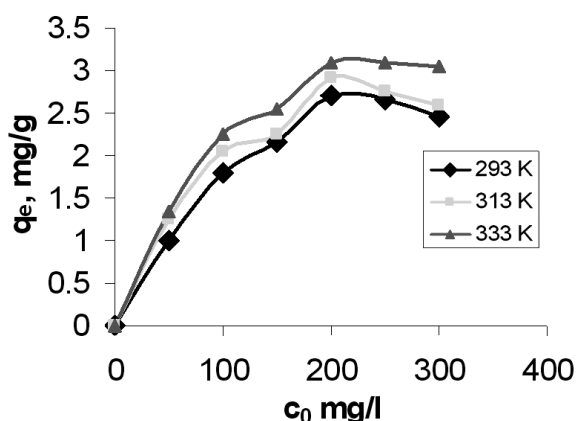
**Figure 1:** Adsorption isotherms of system steel-making slag – Cr(VI) ions
**Slika 1:** Adsorpcijske izoterme sistema jeklarska žlindra – ioni Cr(VI)

0.3 %, MnO – 18 %, $SiO_2$ – 17 %, $Al_2O_3$ – 1.4 %, FeO – 27 %.

## 3 RESULTS AND DISCUSSION

### 3.1 Adsorption isotherms

**Figure 1** shows the adsorption isotherms of Cr(VI) ions on the steel-making slag. The adsorption of Cr(VI) ions on the steel-making slag increased with an increase in the ion concentration. This finding is similar to the other studies.[11,14]

The adsorption-equilibrium data were processed using two isotherms: the Freundlich and Langmuir isotherms. The Langmuir isotherm (Equation 1) and the Freundlich isotherm (Equation 2) can be expressed as:[7,8]

$$q_e = \frac{q_{max} K_L c_e}{1 + K_L c_e} \tag{1}$$

$$q_e = K_F c_e^{1/n} \tag{2}$$

where $c_e$ is the equilibrium concentration of Cr(VI) ions, $q_{max}$ (mg/g) and $q_e$ (mg/g) are the maximum adsorption capacity and the adsorbed amount of Cr(VI) ions. $K_F$
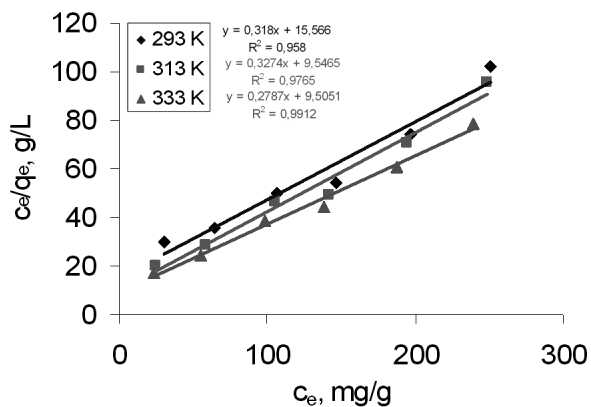
(mg/g) and $n$ are the Freundlich constants. $K_F$ (L/mg) is the adsorption capacity of the adsorbent and $n$ is the intensity of adsorption. $K_L$ is the Langmuir constant related to the energy of adsorption. The parameters of the two isotherms calculated with Equations (1) and (2) are presented in **Table 1** and the fitting curves for the experimental data are shown in **Figures 2** and **3**.

**Table 1:** Parameters of the Langmuir and Freundlich adsorption-isotherm models
**Tabela 1:** Parametri Langmuirovega in Freundlichovega modela adsorpcijskih izoterm

| $T$ K | Langmuir | | | Freundlich | | |
|---|---|---|---|---|---|---|
| | $q_{max}$ mg/g | $K_L$ L/mg | $r^2$ | $n$ | $K_F$ mg/g | $r^2$ |
| 293 | 3.14 | 0.020 | 0.9580 | 2.24 | 0.251 | 0.8678 |
| 313 | 3.05 | 0.034 | 0.9765 | 2.51 | 0.366 | 0.9327 |
| 333 | 3.59 | 0.029 | 0.9912 | 2.80 | 0.930 | 0.9172 |

A comparison of the correlation coefficients and the fitting curves obtained using the two models shows that the Langmuir model was more suitable for the adsorption of Cr(VI) ions from aqueous solutions by the steel-making slag. The Langmuir theory considers the adsorption onto the materials with homogeneous specific surfaces. Therefore, the maximum adsorption capacity ($q_{max}$) can be obtained from the fittings of the adsorption isotherm.[9]

The main feature of the Langmuir adsorption isotherm is a dimensionless constant called the separation factor or equilibrium parameter ($R_L$), presented by the following equation:[15,16]

$$R_L = \frac{1}{1 + K_L c_0} \tag{3}$$

where $c_0$ is the initial concentration of Cr(VI) ions (mg/L). The $R_L$ value indicates the shape of the isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$).[17,18] The $R_L$ value for the studied Cr(VI) ions/steel-making slag system varied from 0.17 to 0.63. It means that the steel-making slag is



**Figure 2:** Langmuir isotherms for the adsorption of Cr(VI) ions by steel-making slag
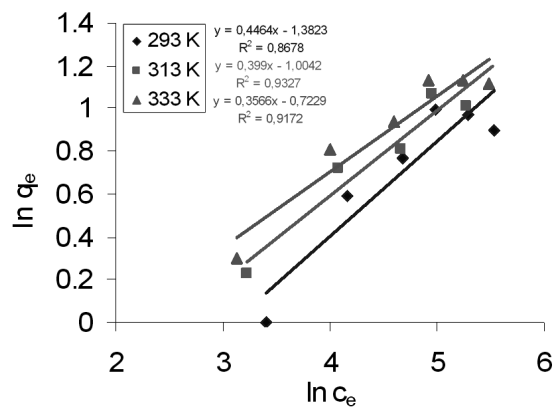**Slika 2:** Langmuirove izoterme adsorpcije ionov Cr(VI) na jeklarsko žlindro



**Figure 3:** Freundlich isotherms for the adsorption of Cr(VI) ions by steel-making slag
**Slika 3:** Freundlichove izoterme za adsorpcijo ionov Cr(VI) na jeklarsko žlindro

**Table 2:** Constants of the adsorption kinetic models (system Cr(VI) ions – steel-making slag)
**Tabela 2:** Konstante kinetičnih modelov adsorpcije (sistem Cr(VI) ioni – jeklarska žlindra)

| Pseudo first order | | Pseudo second order | | Elovich model | | | Intraparticle-diffusion model | | |
|---|---|---|---|---|---|---|---|---|---|
| $k_1$ L/min | $r^2$ | $k_2$ g/(mg min) | $r^2$ | $\beta$ g/mg | $\alpha$ mg/(g min) | $r^2$ | $k_{id}$ h$^{-1}$ | $a$ | $r^2$ |
| 0.121 | 0.9204 | 2.777 | 0.9999 | 1.560 | 2.615 | 0.9061 | 17.227 | 0.340 | 0.8200 |

favorable for the adsorption of Cr(VI) ions from aqueous solutions under the conditions used in this study.

For the Freundlich isotherm, as shown in **Table 1**, $n$ is equal to 2.24. In many cases $n > 1$; this may be a result of the distribution of surface sites or another factor causing a decrease in the adsorbent/adsorbate interaction due to an increase in the surface density.[19] The values of $n$ in the range from 2 to 10 indicate a good adsorption.[20]

### 3.2 Adsorption dynamics

The study of adsorption dynamics describes the rate of solute removal. This rate controls the residence time of the adsorbate uptake at the solid/solution interface. The kinetics of the Cr(VI) ion adsorption on steel-making slag was analyzed using pseudo-first-order, pseudo-second-order, Elovich and intraparticle-diffusion-kinetic models[21–24] (diagram not shown here). The correlation coefficient ($r^2$) indicates the fitting experimental data and the values predicted by the model. A high value of $r^2$ (close or equal to 1) indicates that the model successfully describes the kinetics of the adsorption of Cr(VI) ions.

The pseudo-first-order equation is generally expressed as follows:[15]

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (4)$$

where $q_e$ and $q_t$ are the adsorption capacities at equilibrium and at time $t$, respectively (mg/g), and $k_1$ is the rate constant of the pseudo-first-order adsorption (L/min).

The pseudo-second-order adsorption-kinetic-rate equation is expressed as:[15]

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (5)$$

where $k_2$ is the rate constant of the pseudo-second-order adsorption (g/(mg min)).

The Elovich model equation is generally expressed as:[15]

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \qquad (6)$$

where $\alpha$ is the initial adsorption rate (mg/(g min)) and $\beta$ is the desorption constant (g/mg) during the experiment.

The intraparticle-diffusion model is expressed as:[15]

$$R = k_{id}(t)^a \qquad (7)$$

where $R$ is the percent of the Cr(VI) ions adsorbed, $a$ is the gradient of linear plots and $k_{id}$ is the intraparticle-diffusion-rate constant (h$^{-1}$).

**Figure 4** shows the results of the adsorption capacity of Cr(VI) ions on the steel-making slag versus time at 293 K. The parameters of adsorption-kinetic models are presented in **Table 2**.

The kinetic adsorption of Cr(VI) ions on the steel-making slag followed the pseudo-second-order model (the correlation coefficient ($r^2$) was the highest – 0.9999). The $r^2$ values indicate that the intraparticle-diffusion process is the rate-limiting step. Higher values of $k_{id}$ indicate a better mechanism of adsorption and an increase in the adsorption rate, which is related to an improved bonding between Cr(VI) ions and the adsorbent particles.[24]

### 3.3 Thermodynamic studies

It is necessary to perform thermodynamic studies of the adsorption process to conclude whether the process is spontaneous or not. The Gibbs free energy change ($\Delta G°$) is an important parameter determining the spontaneity of the chemical reaction. In order to determine the Gibbs free energy of the process it is necessary to know the entropy and enthalpy. The reaction occurs spontaneously at a given temperature if $\Delta G°$ has a negative value. The Gibbs free energy change ($\Delta G°$), the enthalpy change ($\Delta H°$) and the entropy change ($\Delta S°$) were calculated from a variation of the thermodynamic equilibrium Langmuir constant, $K_L$. The thermodynamic parameters were calculated using the following equations:[25]

$$\Delta G° = -RT \ln K_L \qquad (8)$$

$$\ln K_L = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \qquad (9)$$
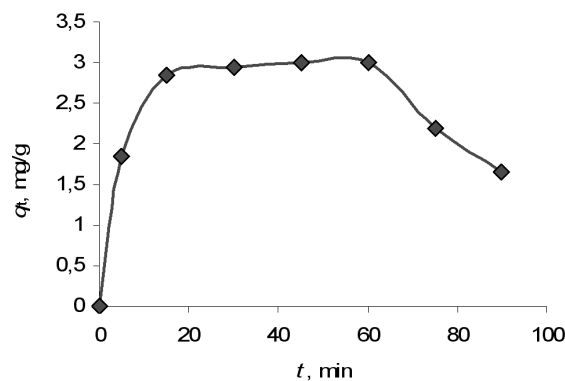


**Figure 4:** Adsorption capacity of Cr(VI) ions on steel-making slag versus time at 293 K
**Slika 4:** Časovna odvisnost kapacitete adsorpcije ionov Cr(VI) na jeklarsko žlindro pri 293 K

where $\Delta H°$ and $\Delta S°$ were determined from the slope and the intercept of the plot of $\ln K_L$ versus $1/T$ (diagram not shown here). Thermodynamic parameters are given in **Table 3**.

**Table 3:** Thermodynamic parameters of the adsorption of Cr(VI) ions on steel-making slag
**Tabela 3:** Termodinamični parametri adsorpcije ionov Cr(VI) na jeklarsko žlindro

| $T$ K | $\Delta G°$, J mol$^{-1}$ | $\Delta H°$, kJ mol$^{-1}$ | $\Delta S°$, J mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|
| 293 313 333 | −9.529 | −3.397 | −2.159 |

A negative value of $\Delta G°$ (**Table 3**) indicates that the adsorption is highly favorable and spontaneous. A negative value of $\Delta H°$ indicates that the adsorption is exothermic. The adsorption in the solid/liquid system consists of two processes: the adsorption of the adsorbate (solute) and desorption of the solvent (water) molecules that have been previously adsorbed. In an endothermic process, to be adsorbed, the adsorbate particles have to displace more than one water molecule. This results in the endothermic reaction of the adsorption process. On the order hand, in an exothermic process, the total energy consumed for bond breaking is lower than the total energy released during the formation of the bond between an adsorbate and an adsorbent. This results in the release of the extra energy in the form of heat. Therefore, $\Delta H°$ will be negative. The value of $\Delta H°$ also indicates the type of adsorption. The heat produced during the physical adsorption is the same as the heats of condensation, i.e., 2.1–20.9 kJ mol$^{-1}$.[26] On the order hand, the heat of chemisorption generally falls into the range of 80–200 kJ mol$^{-1}$.[26] Accordingly, the data in **Table 3** show that the adsorption of Cr(VI) ions can be attributed to the physical-adsorption process. A negative value of $\Delta S°$ indicates that the adsorption process is enthalpy driven. A negative value of the entropy change ($\Delta S°$) also indicates a decreased disorder at the solid/liquid interface during the adsorption process causing the adsorbate ions/molecules to escape from the solid phase to the liquid phase.[26] It this case, there is a decrease in the amount of the adsorbate that can be adsorbed.[27]

## 4 CONCLUSIONS

The present study shows that steel-making slag is an effective adsorbent for a Cr(VI) ion removal from an aqueous solution. The equilibrium studies confirmed that the Langmuir model was better in describing the adsorption of Cr(VI) ions on steel-making slag. The dimensionless-separation factor ($R_L$) showed that steel-making slag could be used for the removal of Cr(VI) ions from an aqueous solution. The amount of the adsorbed Cr(VI) ions increased with an increase in the temperature. The kinetics of the adsorption of Cr(VI) ions on steel-making slag followed a pseudo-second-order model. The $r^2$ values indicate that the intraparticle-diffusion process is

the rate-limiting step. The negative value of $\Delta G°$ indicates that the adsorption is highly favorable and spontaneous. A negative value of $\Delta H°$ indicates that the adsorption is exothermic. A negative value of $\Delta S°$ indicates that the adsorption process is enthalpy driven.

## 5 REFERENCES

[1] B. Zhu, T. X. Fan, D. Zhang, Journal of Hazardous Materials, 153 (**2008**), 300

[2] S. Dahiya, R. M. Tripathi, A. G. Hegde, Journal of Hazardous Materials, 150 (**2008**), 376

[3] N. P. Chermisnoff, Handbook of Water and Wastewater Treatment Technologies, Butterwoth-Heinemann, Boston 2002, 124

[4] G. F. Nordberg, B. A. Fowler, M. Nordberg, L. Friberg, Handbook of Toxicology of Metals, European Environment Agency, Copenhagen 2005, 491

[5] H. Gao, Y. Liu, G. Zeng, W. Xu, T. Li, W. Xia, Journal of Hazardous Materials, 150 (**2007**) 2, 446

[6] I. Lee, Y. Kuan, J. Chern, Journal of the Chinese Institute of Chemical Engineers, 38 (**2007**) 1, 71

[7] K. Kosińska, T. Miśkiewicz, Environment Protection Engineering, 38 (**2012**) 2, 51

[8] A. Štrkalj, A. Rađenović, J. Malina, Journal of Mining and Metallurgy, Section B: Metallurgy, 46 (**2010**) 1, 33

[9] N. C. Kothiyal, S. Sharma, The Holistic Approach to Environment, 3 (**2013**) 2, 63

[10] G. Zhao, X. Wu, X. Tan, X. Wang, The Open Colloid Science Journal, 4 (**2011**), 19

[11] L. Ćurković, M. Trgo, A. Rastovčan-Mioč, N. Vukojević-Medvidović, Indian Journal of Chemical Technology, 16 (**2009**), 84

[12] Manuel AAS ZEEnit 600/650, Analytik Jena AG, Germany, 2006

[13] Perkin-Elmer Corporation, Analitical Methods for Atomic Absorption Spectroscopy, Perkin-Elmer Corporation, USA, 1994, 261

[14] K. Do-Hyung, S. Min-Chul, C. Hyun-Doc, S. Chang-Il, B. Kitae, Desalination, 223 (**2008**), 283

[15] D. Do. Duond, Adsorption Analysis: Equilibria and Kinetics, Imperial College Press, London 1998, 244

[16] K. Hall, L. Eagleton, A. Acrivos, T. Vermeulen, Industrial and Engineering Chemistry Fundamentals, 5 (**1966**) 2, 212

[17] P. K. Malik, Journal of Hazardous Materials, 113 (**2004**) 1–3, 81

[18] P. Pandey, S. S. Sambi, S. K. Sharma, S. Singh, Batch Adsorption Studies for the Removal of Cu(II) Ions by ZeoliteNaX from Aqueous Stream, Proceedings of the World Congress on Engineering and Computer Science, San Francisco, USA, 2009, 20

[19] F. Rouquerol, J. Rouquerol, K. Sing, Adsorption by Powders and Porous Solids, Academic Press, London 1999, 281

[20] A. Ozer, H. B. Pirincci, Journal of Hazardous Materials, 137 (**2006**) 2, 849

[21] Y. S. Ho, D. A. J. Wase, C. F. Forster, Water Research, 29 (**1995**) 5, 1327

[22] C. Chang, C. Chang, K. Chen, W. Tsai, J. Shie, Y. Chen, Journal of Colloid and Interface Science, 277 (**2004**), 29

[23] A. Štrkalj, A. Rađenović, J. Malina, Archives of Metallurgy and Materials, 55 (**2010**) 2, 449

[24] A. Štrkalj, A. Rađenović, J. Malina, Canadian Metallurgical Quarterly, 50 (**2011**) 1, 3

[25] M. Suzuki, Adsorption Engineering, Elsevier Science Publisher, Amsterdam 1990, 300

[26] G. Rosa, H. E. Reynel-Avila, A. Bonilla-Petriciolet, I. Cano-Rodríguez, C. Velasco-Santos, A. L. Martínez-Hernández, International Journal of Chemical and Biological Engineering, 1 (**2008**) 4, 185

[27] D. M. Ruthven, Principles of Adsorption & Adsorption Processes, John Willey and Sons, Inc., Canada 1984, 114