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*I.V. Pylypenko***REMOVAL OF CHROMIUM (VI) FROM AQUEOUS SOLUTIONS BY GRANULAR COMPOSITES BASED ON LAPONITE AND ALGINATE IONOTROPICALLY CROSS-LINKED BY IRON AND ZIRCONIUM IONS****National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute», Kyiv, Ukraine**

The conducted research established the porous structure of the materials through low-temperature nitrogen adsorption. It was demonstrated that the nitrogen sorption isotherms for the investigated samples belong to Type IV with H4 hysteresis associated with bottle-like pores. The specific surface area of the granulated composite samples was determined, ranging from 99 to 111 m<sup>2</sup>/g. Additionally, it was shown that an increase in iron content in the samples leads to a reduction in micropore content. Active centers on the material's surface, primarily composed of hydroxyl groups, were investigated using infrared spectroscopy. The kinetics of chromium (VI) adsorption were explored, and it was established that the iron-to-zirconium ratio in the reinforcement solutions hardly affects the duration of establishing adsorption equilibrium, which is approximately 60 minutes. Pseudo-first-order and pseudo-second-order models were applied to describe the kinetics of the adsorption process. The dependence of the chromium (VI) removal efficiency on the solution pH was determined. It was demonstrated that the synthesized samples exhibited high adsorption in acidic conditions with a sharp decline when transitioning to neutral and alkaline environments. It was shown that the maximum sorption capacities of the synthesized granulated composite samples significantly depend on the ratio of iron and zirconium ions. One of the most efficient samples is that with 50% Fe and 50% Zr, exhibiting a maximum sorption capacity of 13.29 μmol/g at pH 6. The use of Langmuir and Freundlich models allowed establishing the fundamental adsorption properties of the materials.

**Keywords:** chromium (VI), granular composites, laponite; alginate, ionotropically cross-linked, iron ions, zirconium ions, adsorption.

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**Introduction**

Chromium(VI) contamination in water sources has become a significant environmental concern due to its toxic effects on human health and ecosystems. Exposure to high concentrations of chromium (VI) can lead to severe health issues, including cancer and various other detrimental effects. Thus, the development of efficient and cost-effective methods for removing chromium (VI) from aqueous solutions is of paramount importance [1].

In recent years, composite materials have gained considerable attention for their potential applications in water treatment processes [2]. The synergistic

combination of different materials results in enhanced adsorption properties, thereby facilitating the removal of contaminants from water. Laponite, a synthetic layered silicate clay, and alginate, a biopolymer derived from algae, have individually demonstrated promising adsorption capabilities for various pollutants [3–6].

This research presents a novel approach to remove chromium (VI) from aqueous solutions using granular composites based on laponite and alginate. The granular composites are ionotropically cross-linked by iron and zirconium ions, which provide additional binding sites for chromium (VI) adsorption. The incorporation of these metal ions into the composite structure aims

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*Removal of chromium (VI) from aqueous solutions by granular composites based on laponite and alginate ionotropically cross-linked by iron and zirconium ions*

to enhance the overall adsorption capacity and selectivity towards chromium (VI) ions.

The use of laponite and alginate as base materials offers several advantages. Laponite possesses a high surface area and a unique layered structure, providing ample sites for adsorption. Alginate, on the other hand, offers excellent gel-forming properties and biocompatibility, making it an ideal candidate for composite fabrication. The combination of these materials presents a synergistic effect that enhances the composite's adsorption performance. The objectives of this study are threefold: (1) to investigate the synthesis and characterization of the granular composites based on laponite and alginate cross-linked by iron and zirconium ions, (2) to evaluate the adsorption efficiency of the composites towards chromium (VI) ions, and (3) to explore the underlying mechanisms governing the adsorption process.

The findings of this study are expected to contribute to the development of efficient and sustainable solutions for chromium (VI) removal from aqueous solutions. Moreover, the insights gained from the study will aid in further optimizing composite materials and their potential application in other water treatment scenarios.

### **Experimental**

#### *Materials*

In the study, hexahydrate of iron(III) chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), octahydrate of zirconium oxychloride ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ), Laponite RD (cation exchange capacity (CEC) of 0.7 mmol/g), and sodium alginate (Sigma-Aldrich, Germany) were used. Potassium bichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ , Sigma-Aldrich, Germany) was used to prepare solutions of different concentrations of chromium (VI), and HCl and NaOH solutions were used for pH adjustment.

#### *Methods*

The following procedure was used for the synthesis of granulated composites [7]. A 1.5% (w/w) sodium alginate solution was mixed with a 1.5% (w/w) Laponite suspension and stirred for 3 hours. The resulting suspension was added dropwise to strengthening solutions based on 0.1 M solutions of iron chloride, zirconium oxychloride, and their mixture at molar ratios of ions (Fe 75%:Zr 25%; Fe 50%:Zr 50%; and Fe 25%:Zr 75%). The samples were left in the strengthening solutions for 24 hours, rinsed several times with distilled water, and stored in distilled water until further use. The synthesized samples were labeled as  $\text{Fe}_x\text{Zr}_y$ , where «x» represents the amount of iron (III) and «y» represents the amount of zirconium in the strengthening solutions.

The physicochemical properties of the samples were examined using various methods. The data on the pore structure of the samples were determined

based on low-temperature nitrogen adsorption using a NOVA-2200 instrument (Quantachrome, USA). Before the measurements, the samples underwent a degassing stage at a temperature of 100°C (0.0134 Pa) for 20 hours. The specific surface area ( $S_{\text{BET}}$ ) of the samples was calculated using the Brunauer-Emmett-Teller (BET) method. The pore size distribution was determined using the Barrett-Joyner-Halenda (BJH) method. The t-Plot method was used to estimate the micropore volume ( $V_{\mu,t}$ ). The total pore volume ( $V_{\Sigma}$ ) was calculated at the maximum volume of nitrogen adsorbed at a relative pressure of  $p/p_0 \approx 0.99$ , in the volume of liquid nitrogen. The micropore content ( $V_{\mu,\%}$ ) was calculated using the formula  $V_{\mu,\%} = (V_{\mu,t}/V_{\Sigma}) \cdot 100\%$ .

ATR-FTIR spectra of samples were obtained by using QATAR-10 single reflectance FTIR (Shimadzu, Kyoto, Japan) in the wavelength range from 400 to 4000  $\text{cm}^{-1}$ .

The adsorption properties of the materials were determined by bringing 0.25 g of the material into contact with 50  $\text{cm}^3$  of chromium (VI) solution with corresponding concentrations and pH of the solution. The contact time between the solid and liquid phases was 300 min with continuous shaking on an orbital shaker. The pH of the solutions was adjusted by adding solutions of HCl or NaOH of varying concentrations. To investigate the dependence of the sorption capacity on the pH of the solution, an initial chromium (VI) concentration of 100  $\mu\text{mol}/\text{dm}^3$  was used. After reaching the adsorption equilibrium, the residual content of chromium (VI) was determined spectrophotometrically using a UNICO-UV 2100 spectrophotometer (United Products & Instruments, USA) and the diphenylcarbazide method at a wavelength of 540 nm [8].

#### **Results and discussion**

Low-temperature nitrogen adsorption is an important method for evaluating the porous structure of materials. For the investigated samples (Fig. 1), a rather complex nature of nitrogen sorption isotherms is observed. According to the IUPAC classification, the obtained isotherms can be attributed to Type IV, and the presence of hysteresis loops can also be classified as Type IV (H4) [9].

The desorption branches do not connect with the adsorption branches in the region of medium and low pressures. Such behavior is typical for microporous samples with a complex structure of bottle-like pores, where the desorption of nitrogen molecules is complicated. This may indicate the presence of narrow sections in the pore channels. The application of adsorption models (BJH, DFT, etc.) allows for the calculation of the porous structure parameters. The calculated values are presented in Table 1.

Table 1

Characteristics of the porous structure of the samples

Sample	$S_{\text{BET}}$ , m <sup>2</sup> /g	$S_{\text{BJH}}$ , m <sup>2</sup> /g	$S_{\text{micro t-method}}$ , m <sup>2</sup> /g	$S_{\text{DR}}$ , m <sup>2</sup> /g	$S_{\text{DFT}}$ , m <sup>2</sup> /g	$V_{\Sigma}$ , cm <sup>3</sup> /g	$V_{\text{micro t-method}}$ , cm <sup>3</sup> /g	$r_{\text{av, HM}}$
Zr100	104.5	8.65	74.8	112.7	122.5	0.055	0.033	1.05
Fe25Zr75	100.0	6.7	73.3	108.7	123.0	0.053	0.032	1.05
Fe50Zr50	99.3	11.5	61.6	107.0	114.7	0.056	0.027	1.13
Fe75Zr25	111.8	13.7	59.3	127.0	121.1	0.065	0.026	1.17
Fe100	4.0	2.6	–	10.4	5.1	0.006	–	2.90

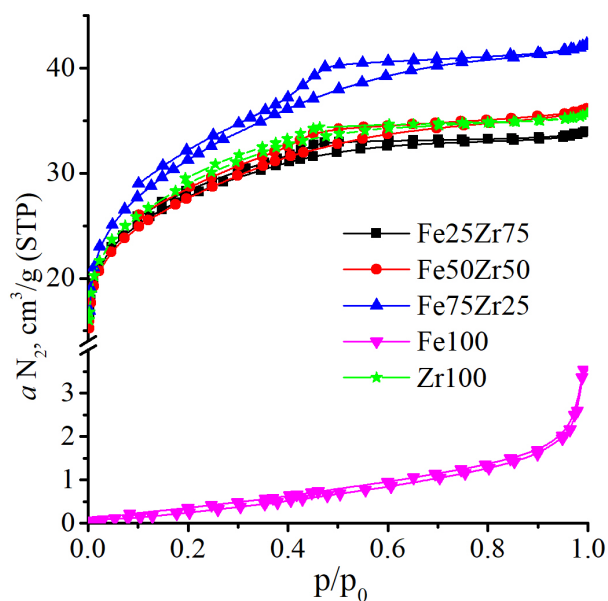


Fig. 1. Adsorption-desorption isotherms of nitrogen on composite samples

The results of nitrogen sorption isotherm calculations using different models indicate a relatively similar pore structure of the investigated samples. The specific surface area, determined by the BET method, varies within the range of 99–111 m<sup>2</sup>/g, except for the Fe100 sample, which exhibits a value of 4 m<sup>2</sup>/g. A slightly larger difference is observed in the calculated specific surface area values obtained using the Dubinin-Radushkevich (DR) method, ranging from 108 to 127 m<sup>2</sup>/g. The specific surface area calculated by the Barrett-Joyner-Halenda (BJH) method shows a greater variation, ranging from 6.7 to 13 m<sup>2</sup>/g. The calculated total pore volume ( $V_{\Sigma}$ ) for the composite samples ranges from 0.026 to 0.033 cm<sup>3</sup>/g. The Zr100 sample exhibits a higher total volume of micropores with a value of 0.033 cm<sup>3</sup>/g, and average pore radius ( $r_{\text{av}}$ ) of 1.05 nm.

The calculation of the micropore content ( $V_{\text{micro t-method}}/V_{\Sigma} \cdot 100$ ) allows for determining the percentage of micropores in the samples. In the composite samples, a decrease in micropore content is observed with increasing iron content: Zr100 (60%),

Fe25Zr75 (61%), Fe50Zr50 (48%), and Fe75Zr25 (40%). This change may be attributed to a more intensive interaction between Fe<sup>3+</sup> ions and alginate molecules, improved diffusion within the granule volume, and the formation of a denser composite structure, unlike Zr<sup>4+</sup> ions, which are more prone to hydrolysis and the formation of large-sized polynuclear complexes. It is likely that such zirconium complexes react predominantly with alginate molecules in the surface layers of the granules, leading to the formation of a dense structure and hindering further ion diffusion within the granule volume [10].

The application of IR spectroscopy enables the determination of the structural features of the synthesized material at the molecular level and, to some extent, its chemical composition. ATR-FTIR spectrum indicates the presence of various types of active centers on the material's surface in the form of hydroxyl and carboxyl groups (Fig. 2). In the high wavenumber region, two prominent bands are observed at 3739 cm<sup>-1</sup> and 3611 cm<sup>-1</sup>. These bands indicate the presence of hydroxyl groups (–OH), suggesting the existence of water molecules and hydroxyl groups associated with the material matrix. Transitioning to the mid-wavenumber region, several important bands are observed. The band at 2358 cm<sup>-1</sup>, along with the band at 2325 cm<sup>-1</sup>, can be attributed to the stretching vibrations of adsorbed water molecules. These bands confirm the presence of water in the material and its involvement in the overall structure and behavior of the material. Another noticeable band in the mid-wavenumber region is observed at 1635 cm<sup>-1</sup>, corresponding to the deformation vibrations of water molecules. This further confirms the presence of water and its contribution to the material's properties. The bands at 1587 and 1417 cm<sup>-1</sup> indicate the stretching vibrations of the C=O bond in alginate. In addition, the band at 1022 cm<sup>-1</sup> corresponds to the stretching vibrations of siloxane bonds Si–O–Si, which belong to Laponite. At the low wavenumber region, the bands at 656 cm<sup>-1</sup> and 632 cm<sup>-1</sup> are likely associated with the deformation vibrations of metal–oxygen (M–O) bonds, possibly related to the presence of Fe(III) and Zr(IV) ions in the composite, which are partially hydrolyzed. These metal ions provide unique chemical

properties to the hydrogel, such as enhanced stability or adsorption capacity. Finally, the band at  $418\text{ cm}^{-1}$  corresponds to the deformation vibrations of siloxane bonds Si–O–Si [11,12].

For granulated samples of any adsorbents, the adsorption kinetics is one of the important parameters. The granule size, porosity, and structure of the sample significantly affect the rate of adsorbate penetration into the granule volume. Diffusion processes depend to a large extent on both the state of the adsorbent and the physicochemical properties of the adsorbate. The obtained results indicate a slight difference in establishing adsorption equilibrium for granular composite samples (Fig. 3) during the removal of chromium (VI) by composite samples. For chromium (VI), the characteristic time of establishing adsorption equilibrium is approximately 60 minutes.

The kinetic dependences (Fig. 3) are described using two kinetic models: pseudo-first-order

$$Q_t = Q_e (1 - e^{-k_1 t})$$

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t}$$

models. Here,  $k_1$  is the rate constant for the pseudo-first-order model;  $Q_e$  and  $Q_t$  are the sorption capacity at equilibrium and at time  $t$ , respectively; and  $k_2$  is the rate constant for the pseudo-second-order model. The calculated model coefficients are presented in Table 2.

It has been established that the experimental data are equally well described by the presented models, as evidenced by the close values of the correlation coefficients  $R^2$ . This allows the use of pseudo-first-order and pseudo-second-order models to describe the chemical stage of the sorption process. Within the pseudo-second-order kinetic model, the rate constants of the process were calculated (Table 2). The rate constants for the pseudo-first-order kinetics are higher. This may be attributed to the significant time required to establish equilibrium in the system (approximately 1 hour). In the pseudo-second-order

model, the rate of the adsorption process is determined by the rate of the chemical interaction stage between the sorbate and the sorbent.

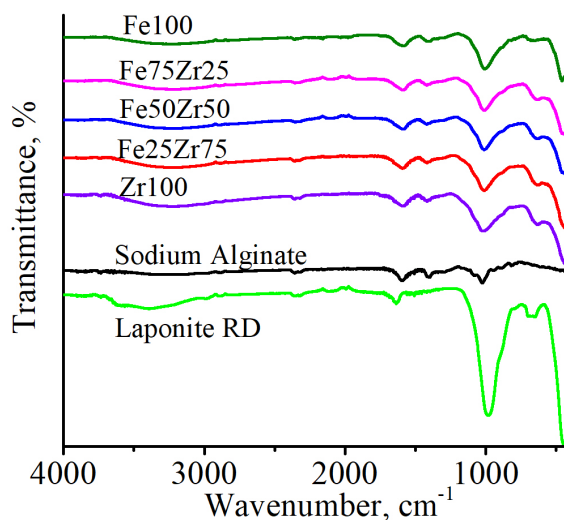


Fig. 2. ATR-FTIR spectra of composite samples

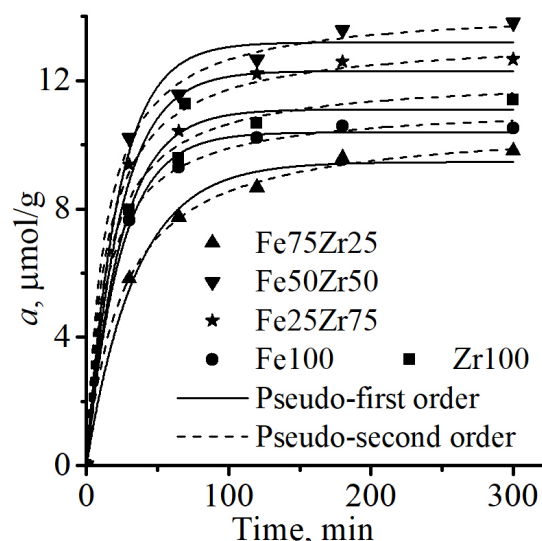


Fig. 3. Kinetics of chromium (VI) sorption by granulated composite samples

Table 2

Parameters of the pseudo-first-order and pseudo-second-order kinetic models for Cr(VI) sorption by granulated composite samples

Sample	Pseudo-first-order model			Pseudo-second-order model		
	$Q_e$ , $\mu\text{mol/g}$	$k_1$ , $\text{min}^{-1}$	$R^2$	$Q_e$ , $\mu\text{mol/g}$	$k_2$ , $\text{g}/\mu\text{mol/g} \cdot \text{min}$	$R^2$
Zr100	11.1	0.041	0.9808	12.1	$5.91 \cdot 10^{-3}$	0.9773
Fe25Zr75	12.3	0.042	0.9822	13.3	$5.43 \cdot 10^{-3}$	0.9947
Fe50Zr50	13.2	0.045	0.9836	14.3	$5.41 \cdot 10^{-3}$	0.9972
Fe75Zr25	9.5	0.028	0.9891	10.7	$3.72 \cdot 10^{-3}$	0.9986
Fe100	10.4	0.042	0.9957	11.2	$6.49 \cdot 10^{-3}$	0.9773

The chromate ions possess a relatively small ionic radius (2.56 Å) and readily diffuse into the sample structure, predominantly adsorbing at the active centers of Fe(III)/Zr(IV). These centers could be ions of iron or zirconium, including partially hydrolyzed forms (e.g., OH–Fe= or OH–Zr=). Such hydroxyl groups are capable of forming surface complexes like Fe–OHCrO<sub>4</sub><sup>−</sup> or other compositions [13]. Additionally, one should not dismiss the reactions forming iron chromates like Fe<sub>2</sub>(CrO<sub>4</sub>)<sub>3</sub> [14,15], or zirconium chromates.

The pH of a solution significantly affects the sorption-based removal processes of heavy metals from aqueous solutions. Through conducted experimental investigations, the influence of pH on the efficiency of chromium (VI) removal from aqueous solutions has been established. For chromium (VI), the curve's shape (Fig. 4a) is characteristic of anions exhibiting higher sorption levels in acidic environments and a sharp decline in sorption within neutral and alkaline environments. This dependence, as known, is associated with the surface chemistry of the adsorbent samples. In an acidic environment, surface hydroxyl and carboxyl groups have the capacity for proton attachment, acquiring a positive charge accordingly. Such positively charged groups (e.g. =S–OH<sub>2</sub><sup>+</sup>) electrostatically interact with chromium (VI) anions, forming so-called surface complexes of diverse composition [13].

Upon transitioning to a neutral or alkaline environment, the concentration of positively charged groups markedly decreases, resulting in a reduction in the adsorption magnitude correspondingly. Conversely, the alteration in the distribution of chromium (VI) forms in the solution may also contribute to the efficiency of removal. The primary forms of hexavalent

chromium are HCrO<sub>4</sub><sup>−</sup> anions up to a pH of 6.5, and in a more alkaline environment, CrO<sub>4</sub><sup>2−</sup> predominates (Fig. 4b).

The sorption isotherms highlight the significant influence of the chemical composition of the composite samples on the sorption magnitude (Fig. 5). Analysis of the obtained results indicates that the sorption properties of the samples vary with changes in the Zr:Fe ratio in the reinforcement solutions. This dependence can be explained by the peculiarities of the hydrolysis processes of iron and zirconium ions during ionotropic reinforcement and their interaction with the OH- and COOH-groups of alginate. The Fe or Zr ions present in the material structure, capable of hydrolysis to form active hydroxyl groups, can complex with chromate anions. Hence, the sorption levels of chromium (VI) will primarily depend on the content and ratio of Fe and Zr in the samples [13].

The application of Langmuir  $a_s = \frac{K_L a_\infty C_e}{1 + K_L C_e}$

and Freundlich  $a_s = K_F C_e^{\frac{1}{n}}$  models to the obtained sorption isotherms allows for the determination of the coefficient values corresponding to the respective equations, as presented in Table 3.

Correlation coefficients R<sup>2</sup> within the range of 0.95–1.00 suggest the applicability of the proposed models in describing the sorption processes of chromium (VI) by granulated composite samples. In most cases, the Langmuir model better describes the experimental data, supported by higher correlation coefficient values compared to the Freundlich model.

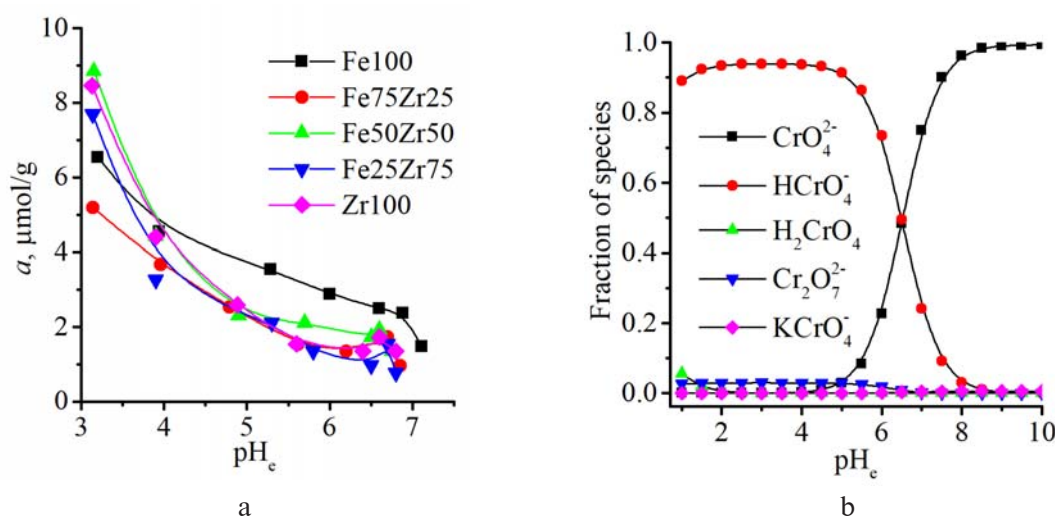


Fig. 4. Chromium (VI) sorption dependence on the pH of the solution for granulated composite samples (a), and the distribution diagram of chromium (VI) forms based on the pH of the aqueous solution (b)

Table 3

Equation coefficients of the chromium (VI) adsorption by granulated composite samples at pH 6

Sample	Freundlich model			Langmuir model		
	$K_F, (\mu\text{mol/g})(\mu\text{mol/L})^n$	n	$R^2$	$K_L, \text{L}/\mu\text{mol}$	$a_\infty, \mu\text{mol/g}$	$R^2$
Fe100	2.73	9.2	0.9616	0.0176	6.15	0.9557
Fe75Zr25	1.13	4.6	0.8741	0.0088	5.78	0.9475
Fe50Zr50	1.75	3.8	0.9396	0.0048	13.29	0.9704
Fe25Zr75	0.65	2.6	0.9608	0.0025	13.16	0.9853
Zr100	2.29	5.9	0.9607	0.0092	8.38	0.9859

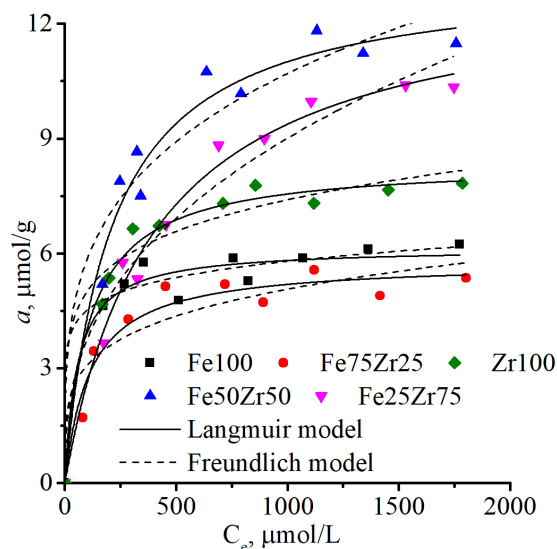


Fig. 5. Sorption isotherms of chromium (VI) on granulated composite samples (pH 6)

For the investigated composite samples, a reduction in the values of the maximum sorption capacity ( $a_\infty$ ,  $\mu\text{mol/g}$ ) and affinity is observed with changing Zr:Fe ratio, as evidenced by variations in the adsorption equilibrium constant ( $K_L$ ). The Freundlich model slightly less effectively describes the sorption isotherms. The  $K_F$  value is associated with the energy of interaction between the adsorbent and adsorbate, and higher values suggest a stronger interaction, indicating higher affinity or, to some extent, selectivity. On the other hand, the coefficient  $n$ , known as the Freundlich exponent or the intensity of adsorption, typically ranges from 1 to 10, representing the extent of adsorption intensity.

Based on the analysis of the obtained data, the most efficient sample for chromium (VI) removal can be determined. Specifically, the sample Fe50Zr50 exhibits the highest maximum sorption capacity ( $a_\infty$ ) at 13.29  $\mu\text{mol/g}$ . Furthermore, considering the magnitude of the adsorption equilibrium constant ( $K_L$ ), one can infer the efficiency of the adsorbent for chromium (VI) removal from solutions of low

concentration since this constant reflects the level of affinity and, to some extent, the binding energy. Following this principle, the most efficient sample for chromium (VI) removal is Fe100 (0.0176  $\text{L}/\mu\text{mol}$ ).

### Conclusions

It has been determined that the synthesized granulated composite samples effectively remove chromium (VI) from aqueous solutions at pH 6 (up to 13.3  $\mu\text{mol/g}$ ). The analysis demonstrates that the composite samples possess a sufficiently developed specific surface area (up to 111  $\text{m}^2/\text{g}$ ); however, their predominant microporosity negatively affects the surface accessibility for chromium (VI) adsorption from aqueous solutions. Further investigations should be focused on enhancing the pore structure of similar materials to increase the content of meso- and macropores, which play a fundamental role in the sorption removal processes of heavy metals from aquatic environments.

### REFERENCES

1. *Recent* advances in removal techniques of Cr(VI) toxic ion from aqueous solution: a comprehensive review / Karimi-Maleh H., Ayati A., Ghanbari S., Orooji Y., Tanhaei B., Karimi F., Sillanpaa M. // *J. Mol. Liq.* – 2021. – Vol.329. – Art. No. 115062.
2. *A systematic* review on adsorptive removal of hexavalent chromium from aqueous solutions: Recent advances / Rajapaksha A.U., Selvasembian R., Ashiq A., Gunarathne V., Ekanayake A., Perera V.O., Ok Y.S. // *Sci. Total Environ.* – 2022. – Vol.809. – Art. No. 152055.
3. *Sorption* of cobalt, chromium and uranium ions on Fe/Ti-pillared montmorillonite / Pylypenko I.V., Spasonova L.M., Kovalchuk I.A., Veremeienko V.V. // *East. Eur. J. Enterprise Technol.* – 2014. – Vol.4. – No. 6. – P.57-61.
4. *Novel* magnetic polyvinyl alcohol/laponite RD nanocomposite hydrogels for efficient removal of methylene blue / Mahdavinia G. R., Soleymani M., Sabzi M., Azimi H., Atlasi Z. // *J. Environ. Chem. Eng.* – 2017. – Vol.5. – No. 3. – P.2617-2630.

5. Use of laponite as adsorbents for Ni(II) removal from aqueous solution / Cao X., Yan B., Huang Y., Zhang Y., Li L., Qiu J., Lyu X. // *Environ. Prog. Sustainable Energy*. – 2018. – Vol.37. – No. 3. – P.942-950.

6. Clay mineral adsorbents for heavy metal removal from wastewater: a review / Gu S., Kang X., Wang L., Lichtfouse E., Wang C. // *Environ. Chem. Lett.* – 2019. – Vol.17. – P.629-654.

7. *Pylypenko I.V.* Granular composites based on laponite and sodium alginate for removal of methylene blue from aqueous solutions // *Sci. Notes Taurida Natl. Vernadsky Univ. Ser. Techn. Sci.* – 2023. – Vol.34. – No. 3. – P.77-84.

8. Method of analysis for determination of the chromium (Cr) species in water samples by spectrophotometry with diphenylcarbazide / Wiryawan A., Retnowati R., Burhan P., Syekhfan S. // *J. Environ. Eng. Sustainable Technol.* – 2018. – Vol.5. – No. 1. – P.37-46.

9. Adsorption by powders and porous solids: principles, methodology and applications / Rouquerol J., Rouquerol F., Llewellyn P., Maurin G., Sing K.S. – London: Academic Press, 2012. – 646 p.

10. Porous zirconium alginate beads adsorbent for fluoride adsorption from aqueous solutions / Qiusheng Z., Xiaoyan L., Jin Q., Jing W., Xuegang L. // *RSC Adv.* – 2015. – Vol.5. – No. 3. – P.2100-2112.

11. Development of new alginate entrapped Fe(III)–Zr(IV) binary mixed oxide for removal of fluoride from water bodies / Swain S.K., Patnaik T., Patnaik P.C., Jha U., Dey R.K. // *Chem. Eng. J.* – 2013. – Vol.215-216. – P.763-771.

12. Iron-zirconium microwave-assisted modification of small-pore zeolite W and its alginate composites for enhanced aqueous removal of As(V) ions: experimental and theoretical studies / Abdellaoui Y., El Ibrahim B., Abou Oualid H., Kassab Z., Quintal-Franco C., Giacoman-Vallejos G., Gamero-Melo P. // *Chem. Eng. J.* – 2021. – Vol.421. – Art. No. 129909.

13. Surface complexation of chromium(VI) on iron(III) hydroxide: mechanisms and stability constants of surfaces complexes / Hmamou M., Maarouf F.E., Ammary B., Bellaouchou A. // *Indones. J. Chem.* – 2021. – Vol.21. – No. 3. – P.679-689.

14. Baron D., Palmer C.D., Stanley J.T. Identification of two iron–chromate precipitates in a Cr(VI)-contaminated soil // *Environ. Sci. Tech.* – 1996. – Vol.30. – No. 3. – P.964-968.

15. Precipitation equilibria of the chromium(VI)/iron(III) system and spectroscopic characterization of the precipitates / Olazabal M.A., Nikolaidis N.P., Suib S.A., Madariaga J.M. // *Environ. Sci. Tech.* – 1997. – Vol.31. – No. 10. – P.2898-2902.

## ВИЛУЧЕННЯ ХРОМУ(VI) З ВОДНИХ РОЗЧИНІВ ГРАНУЛЬОВАНИМИ КОМПОЗИТАМИ НА ОСНОВІ ЛАПОНІТУ ТА АЛЬГІНАТУ, ІОНОТРОПНО ЗМІЩЕНИХ ІОНАМИ ЗАЛІЗА ТА ЦИРКОНІЮ

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За допомогою методу низькотемпературної адсорбції азоту встановлено пористу структуру матеріалів. Показано, що ізотерми сорбції азоту відносяться до IV типу та гістерезисом H4 з пляшкоподібними порами. Визначена питома площа поверхні зразків гранульованих композитів, яка коливається від 99 до 111 м<sup>2</sup>/г. Доведено, що із збільшенням вмісту заліза в зразках спостерігається зменшення вмісту мікропор. За допомогою ІЧ-спектроскопії досліджено активні центри на поверхні матеріалу, які складаються, переважно, з гідроксильних груп. Досліджено кінетику адсорбції хрому(VI) та встановлено, що співвідношення заліза та цирконію у розчинах зміцнення практично не впливає на тривалість встановлення адсорбційної рівноваги, який складає приблизно 60 хвилин. Моделі псевдопершого та псевдодругого порядку застосовано для опису кінетики процесу сорбції. Встановлено залежність ефективності вилучення хрому(VI) від рН розчину. Показано, що синтезовані зразки мають високі величини сорбції в кислому середовищі з достатньо різким зниженням при переході до нейтрального та лужного середовища. Показано, що величини граничної адсорбції синтезованих зразків гранульованих композитів суттєво залежать від співвідношення іонів заліза та цирконію. Одним з найефективніших є зразок з 50% Fe та 50% Zr з величиною граничної адсорбції 13,29 мкмоль/г при рН 6. Застосування моделей Ленгмюра та Фрейндліха до одержаних даних дозволило встановити основні адсорбційні властивості матеріалів.

**Ключові слова:** хром(VI), гранульовані композити, лaponit, альгінат, іонотропно зміцнені, іони заліза, іони цирконію, адсорбція.

## REMOVAL OF CHROMIUM (VI) FROM AQUEOUS SOLUTIONS BY GRANULAR COMPOSITES BASED ON LAPONITE AND ALGINATE IONOTROPICALLY CROSS-LINKED BY IRON AND ZIRCONIUM IONS

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The conducted research established the porous structure of the materials through low-temperature nitrogen adsorption. It was demonstrated that the nitrogen sorption isotherms for the investigated samples belong to Type IV with H4 hysteresis associated with bottle-like pores. The specific surface area of the granulated composite samples was determined, ranging from 99 to 111 m<sup>2</sup>/g. Additionally, it was shown that an increase in iron content in the samples leads to a reduction in micropore content. Active centers on the material's surface, primarily composed of hydroxyl groups, were investigated using infrared spectroscopy. The kinetics of chromium (VI) adsorption were explored, and it was established that the iron-to-zirconium ratio in the reinforcement solutions hardly affects the duration of establishing adsorption equilibrium, which is approximately 60 minutes. Pseudo-first-order and pseudo-second-order models were applied to describe the kinetics of the adsorption process. The dependence of the chromium (VI) removal efficiency on the solution pH was determined. It was demonstrated that the synthesized samples exhibited high adsorption in acidic conditions with a sharp decline

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when transitioning to neutral and alkaline environments. It was shown that the maximum sorption capacities of the synthesized granulated composite samples significantly depend on the ratio of iron and zirconium ions. One of the most efficient samples is that with 50% Fe and 50% Zr, exhibiting a maximum sorption capacity of 13.29  $\mu\text{mol/g}$  at pH 6. The use of Langmuir and Freundlich models allowed establishing the fundamental adsorption properties of the materials.

**Keywords:** chromium (VI); granular composites; laponite; alginate; ionotropically cross-linked; iron ions; zirconium ions; adsorption.

#### REFERENCES

1. Karimi-Maleh H, Ayati A, Ghanbari S, Orooji Y, Tanhaei B, Karimi F, et al. Recent advances in removal techniques of Cr(VI) toxic ion from aqueous solution: a comprehensive review. *J Mol Liq.* 2021; 329: 115062. doi: 10.1016/j.molliq.2020.115062.
2. Rajapaksha AU, Selvasembian R, Ashiq A, Gunarathne V, Ekanayake A, Perera VO, et al. A systematic review on adsorptive removal of hexavalent chromium from aqueous solutions: recent advances. *Sci Total Environ.* 2022; 809: 152055. doi: 10.1016/j.scitotenv.2021.152055.
3. Pylypenko IV, Spasonova LM, Kovalchuk IA, Veremeienko VV. Sorption of cobalt, chromium and uranium ions on Fe/Ti-pillared montmorillonite. *East Eur J Enterprise Technol.* 2014; 4(6): 57-61. doi: 10.15587/1729-4061.2014.26246.
4. Mahdavinia GR, Soleymani M, Sabzi M, Azimi H, Atlasi Z. Novel magnetic polyvinyl alcohol/laponite RD nanocomposite hydrogels for efficient removal of methylene blue. *J Environ Chem Eng.* 2017; 5: 2617-2630. doi: 10.1016/j.jece.2017.05.017.
5. Cao X, Yan B, Huang Y, Zhang Y, Li L, Qiu J, et al. Use of laponite as adsorbents for Ni(II) removal from aqueous solution. *Environ Prog Sustainable Energy.* 2018; 37: 942-950. doi: 10.1002/ep.12749.
6. Gu S, Kang X, Wang L, Lichtfouse E, Wang C. Clay mineral adsorbents for heavy metal removal from wastewater: a review. *Environ Chem Lett.* 2019; 17: 629-654. doi: 10.1007/s10311-018-0813-9.
7. Pylypenko IV. Hranulovani kompozyty na osnovi laponitu ta alhinatu natriuu dlia vyluchennia metylenovoho blakytynoho z vodnykh rozchyniv [Granular composites based on laponite and sodium alginate for the extraction of methyl blue from aqueous solutions]. *Vcheni Zapysky TNU imeni V.I. Vernadskogo. Seriya: Tekhnichni Nauky.* 2023; 34(3): 77-84. (in Ukrainian). doi: 10.32782/2663-5941/2023.3.2/13.
8. Wiryawan A, Retnowati R, Burhan P, Syekhiani S. Method of analysis for determination of the chromium (Cr) species in water samples by spectrophotometry with diphenylcarbazide. *J Environ Eng Sustainable Technol.* 2018; 5(1): 37-46. doi: 10.21776/ub.jeest.2018.005.01.6.
9. Rouquerol J, Rouquerol F, Llewellyn P, Maurin G, Sing KS. *Adsorption by powders and porous solids: principles, methodology and applications.* London: Academic Press; 2012. 646 p. doi: 10.1016/C2010-0-66232-8.
10. Qiusheng Z, Xiaoyan L, Jin Q, Jing W, Xuegang L. Porous zirconium alginate beads adsorbent for fluoride adsorption from aqueous solutions. *RSC Adv.* 2015; 5: 2100-2112. doi: 10.1039/C4RA12036A.
11. Swain SK, Patnaik T, Patnaik PC, Jha U, Dey RK. Development of new alginate entrapped Fe(III)-Zr(IV) binary mixed oxide for removal of fluoride from water bodies. *Chem Eng J.* 2013; 215-216: 763-771. doi: 10.1016/j.cej.2012.10.098.
12. Abdellaoui Y, El Ibrahimy B, Abou Oualid H, Kassab Z, Quintal-Franco C, Giacomani-Vallejos G, et al. Iron-zirconium microwave-assisted modification of small-pore zeolite W and its alginate composites for enhanced aqueous removal of As(V) ions: experimental and theoretical studies. *Chem Eng J.* 2021; 421: 129909. doi: 10.1016/j.cej.2021.129909.
13. Hmamou M, Maarouf FE, Ammary B, Bellaouchou A. Surface complexation of chromium(VI) on iron(III) hydroxide: mechanisms and stability constants of surfaces complexes. *Indones J Chem.* 2021; 21(3): 679-689. doi: 10.22146/ijc.60634.
14. Baron D, Palmer CD, Stanley JT. Identification of two iron-chromate precipitates in a Cr(VI)-contaminated soil. *Environ Sci Tech.* 1996; 30: 964-968. doi: 10.1021/es9504348.
15. Olazabal MA, Nikolaidis NP, Suib SA, Madariaga JM. Precipitation equilibria of the chromium(VI)/iron(III) system and spectroscopic characterization of the precipitates. *Environ Sci Tech.* 1997; 31: 2898-2902. doi: 10.1021/es9700865.