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ADSORPTION OF Cr(VI) BY POLYANILINES AND CELLULOSE/POLYANILINE COMPOSITES SYNTHESIZED IN AQUEOUS SOLUTIONS OF CARBOXYLIC ACIDS

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Samples of polyaniline (PAn) and cellulose/polyaniline composites (Cel/PAn), obtained by oxidative polymerization of aniline in aqueous 0.5 M solutions of carboxylic acids (formic, acetic, oxalic, and citric), were used to study the adsorption of Cr(VI) from model aqueous solutions. The ratio of aniline : cellulose in the synthesis of Cel/PAn composites was 1 : 1 (g : g). Polyaniline in both PAn and Cel/PAn samples after synthesis was in the form doped with carboxylic acids.

Based on the results of adsorption studies, kinetic curves of Cr(VI) adsorption from aqueous solutions with concentrations of 100, 200, 330 and 400 mg/L by PAn samples and samples of Cel/PAn composites were constructed. The study of the kinetics of adsorption by PAn samples from solutions with Cr(VI) concentrations of 100 and 200 mg/L showed that the process is one-stage, and at concentrations of 330–400 mg/L it is two-stage. Adsorption of Cr(VI) from solutions with concentrations of 100, 200, 330 and 400 mg/L by Cel/PAn samples is a two-stage process.

The adsorption capacity of both PAn samples and Cel/PAn composites depends on the concentration of Cr(VI) in the initial solutions. An increase in the initial concentration of Cr(VI) in the solutions leads to an increase in the values of adsorption values both at the first stage and at the second stage of the process by both PAn samples and Cel/PAn samples. The course of the second stage of the adsorption process, which obviously includes sorption, is longer, however, it is during this stage that the maximum values of the adsorption capacities for Cr(VI) are reached.

According to the research results, Langmuir and Freundlich isotherms were constructed. It was established that the process of Cr(VI) adsorption by PAn and Cel/PAn samples, in which PAn doped with various organic acids, best agrees with the Langmuir adsorption model.

Electron spectroscopy (ES), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) microanalysis, and elemental mapping (EC) were used to study adsorption.

Keywords: polyaniline, composites, cellulose/polyaniline, carboxylic acids, adsorption, chromium(VI).

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1. Introduction

A wide range of physicochemical properties of polyaniline (PAn), unique among which are the strict orderliness of the structure, a multitude of form-states, the ability to

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quickly change these form-states, economy, variety and simplicity of synthesis methods, and the morphology of the obtained particles [1] make PAn attractive material for various uses in modern technologies [2, 3]. However, despite the variety of synthesis methods and a wide range of physicochemical properties, PAn is a fragile, powdery polymer. For effective application of PAn, in many cases it is applied to various matrices-carriers of both inorganic [3] and organic polymeric nature [4]. Due to its high affinity to the surfaces of various materials, PAn perfectly combines with matrix carriers due to the formation of hydrogen bonds (H-bonds). Excellent candidates for creating such composites are biopolymers, such as lignocellulose [5, 6] and cellulose (Cel) [7, 8]. The value of Cel, the most common biopolymer in nature, lies in the wealth of sources of renewal. The annual volume of pulp production is estimated at 100 billion tons [9]. Data Bridge market research shows that the global pulp market, which was 40.56 billion USD in 2022, will grow to 93.10 billion USD by 2030 [10]. One of the important applications of Cel is the creation of composite materials (CMs), which are used as adsorbents for the purification of water of various origins from heavy metals (HMs) and dyes [11]. The removal of HMs from both wastewater and natural waters is an extremely urgent problem today [1, 11–13].

Heavy metals include chemical elements with an atomic weight in the range from 63.5 to 200.6 a.o.m. and with a specific gravity of more than 5.0 g/cm^3 [12]. Pollution of the environment by HM and chromium, in particular, has increased over the past few decades, especially in developing countries. The growth of battery production, fertilizer production, anticorrosion protection of metals, mining, leather processing, etc. is the reason for the increase in environmental pollution. It is important that HMs are not subject to biological decomposition and are able to accumulate in living organisms. They have toxic or carcinogenic properties and are dangerous pollutants for the environment and humans in particular. Mercury, cadmium, lead, copper, zinc, nickel, and chromium, as toxic metals, are the main problem in industrial wastewater treatment [14].

Chromium (Cr) is the first in the list of carcinogenic substances and ranks fifth among potentially toxic elements [15]. Chromium as a geochemical element is common in almost all natural objects [16]. In the natural environment, chromium exists mainly in two oxidation states Cr(VI) and Cr(III). Cr(VI) is highly soluble, mobile and toxic to humans, animals and plants. On the contrary, Cr(III) is practically insoluble, has low toxicity and, unlike Cr(VI), is necessary in trace amounts in human food. Cr(III) is usually found in the form of $Cr(OH)_3$ or Cr(III) in complexes with organic ligands [17]. It is important that at concentrations of Cr(VI) over 300 mg L^{-1} and at pH 1–6.5 $Cr_2O_7^{2-}$ is mostly present in aqueous solutions [18].

For the utilization of chromium compounds from waters of various origins, CMs based on Cel and PAn [19, 20], which are synthesized by chemical oxidation of aniline mainly in aqueous solutions of various acids in the presence of dispersed Cel, can be extremely useful [1, 21]. The synthesis of such composites by the in situ method is of great practical importance. After all, this greatly simplifies the methods of combining the properties of Cel and PAn, and as a result, new materials with interesting physicochemical properties are formed [22]. Cel macromolecules contain many hydroxyl groups, which increase favorable conditions for grafting various polymers [19, 20]. Hydroxyl groups of Cel can act not only as electron donors for the reduction of Cr(VI), but also as active centers for the precipitation and retention of Cr(III) [1, 21]. Adsorption is the most common method of removing HM and Cr(VI), in particular, from aqueous solutions due to the ease of implementation of the process, a wide selection of adsorbents, low cost, high efficiency, and the possibility of reusing adsorbents [22–24]. Microcomposite adsorbents of the Cel/PAn type have a number of disadvantages compared to nanocomposite Cel/PAn adsorbents. The main one is the significantly lower adsorption capacity of microcomposites. However, this can be a significant advantage of such composites over nanocomposites. The synthesis process of microcomposite adsorbents is much cheaper and easier to work with [25]. As is known, nanocomposites, especially adsorbents, require special conditions of use for removal from water purified from HMs after adsorption [26]. Insufficient purification of water from nanoparticle residues can be harmful to both people [27, 28] and plants [29, 30]. The use of composites based on microfibrillar Cel and PAn significantly simplifies the process of adsorption of HMs, in particular Cr(VI), and utilization of adsorbed chromium. Under the conditions of optimal selection of the ratio of aniline: cellulose deposited on the surface of PAn microfibrils, it can form nanolayers of nanoaggregates of polyaniline macromolecules [31].

Microfibrillar Cel is an extremely popular component of various CMs [32]. Deposition of PAn on the surface of Cel microfibrils in situ in aqueous solutions of carboxylic acids occurs with high efficiency and degree of filling of the surface of cellulose microfibrils [33]. Carboxylic acids used in the synthesis of PAn and Cel/PAn composites, due to their structure, can enhance intermolecular interaction and increase the chemical affinity of the components in Cel/PAn composites. Samples of composites containing Cel and PAn doped with various carboxylic acids are also interesting from the point of view of their environmental friendliness for use as Cr(VI) adsorbents.

Research and comparison of Cr(VI) sorption properties of PAn samples and microfibrillar Cel/PAn composites obtained in solutions of formic acid, acetic acid, oxalic acid, and citric acid is the subject of this study. An interesting aspect of the use of PAn samples and Cel/PAn composites is that the study of Cr(VI) adsorption from aqueous solutions was carried out without their acidification with acids.

2. Experimental section

2.1. Reactants and materials

The samples of PAn and composites of Cel/PAn were synthesized by chemical oxidative polymerization of aniline (An) using ammonium peroxodisulphate (APS), “Aldrich”, formic acids (FA), acetic acids (AA), oxalic acids (OA), citric acids (CA) and mixture of microfibrillar celluloses, namely TM Linters ADM, USA, melt pulp 1290 µm, viscosity 37050 mPa·s, degree of polymerization (DP=2050) and two samples of celluloses, TM Biofloc (HV+, MV), melt pulp 1 290 µm, viscosity 24700 and 10530 mPa·s (TM Tember, Canada) and degree of polymerizations 1400 and 1150, in mass ratio (in %) 50.0:37.5:12.5 accordingly (conditional designation – Cel). Distilled water was used as solvent.

2.2. Synthesis of PAn and composites Cel/PAn

A portion of An (1 g) was dissolved in 80 ml of 0,5 M aqueous solution of formic, acetic, oxalic, or citric acid. Afterwards 2.68 g of APS was also dissolved in 20 mL of 0.5 M solutions of above-mentioned acids. Dropwise was added solution of APS for one hour and then further stirred for one hour. Obtained suspension was left for 24 h, filtered and washed with distilled water until the filtrate was neutral [34].

For the synthesis of composites Cel/PAn sample of An (1 g) was dissolved in 80 ml of 0.5 M aqueous solution of formic, acetic, oxalic, or citric acids and simultaneously a sample of APS (2.68 g) was dissolve in 20 mL of 0.5 M solutions of the above-mentioned carboxylic acids. Then to the solution of aniline was added 1 g of Cel and stirred for one hour, following the solution of APS was added dropwise over the second hour and finally stirred for one hour. Composites were washed and isolated as PAn [33, 34].

2.3. Preparation for investigation

The synthesized samples were dried in a vacuum oven at 50 °C and liquefied by 0.9 кG·см$^{-2}$, after that pulverised and implemented for research of physicochemical and adsorption properties. During the synthesis, polyaniline in obtained PAn and Cel/PAn samples was doped by carboxylic acid (CXA) [33, 34].

2.4. Research methods

Morphology, surface topology, energy dispersive X-ray (EDX) microanalysis and elemental mapping – distribution of chemical elements of adsorbents were studied using a scanning electron microscope (TESCAN VEGA3). Electronic spectra of adsorptive solutions were recorded using a Cadas-100 spectrophotometer.

2.5. Methods of adsorption research

Cr(VI) adsorption was studied under static conditions at a temperature of 20±1 °C. Weighing samples of adsorbent (PAn, composites Cel/PAn and Cel) were filled with 10 mL of Cr(VI) solution with concentrations (100 or 200, or 330, or 400) mg/L and the time of the start of adsorption was recorded. After certain time intervals, samples were taken and spectra were recorded in the range of 350–600 nm with a step of 10 nm. The band of the absorption spectrum at 350 nm served as the working one. The thickness of the quartz cuvette was 2 mm. After photometry, the analyzed solutions were re-introduced into the Cr(VI) adsorbent system. The working volume of the solution remained constant all the time (10 ml). The amount of adsorbed substance was determined by the calibration curve. The adsorption (A_t) of Cr(VI) from the solution during a certain time of the process was calculated according to the equation:

$$A_t = (C_0 - C_t)\, V / m, \qquad (1)$$

where: A_t – is the amount of Cr(VI) adsorbed during time (t), mg/g; C_0 – initial concentration of Cr(VI), mg/L; C_t – concentration of Cr(VI) at a specific time, mg/L; V – solution volume, L; m – is the mass of the adsorbent, g.

For the description of adsorption, the most common are mathematical models of Langmuir and Freundlich isotherms [35], respectively:

$$\frac{1}{A_t} = \frac{1}{A_{\max}} + \frac{1}{A_{\max} K_L C_t}\ , \qquad (2)$$

$$\ln A_t = \ln K_F + \frac{1}{n_F} \ln C_t\ , \qquad (3)$$

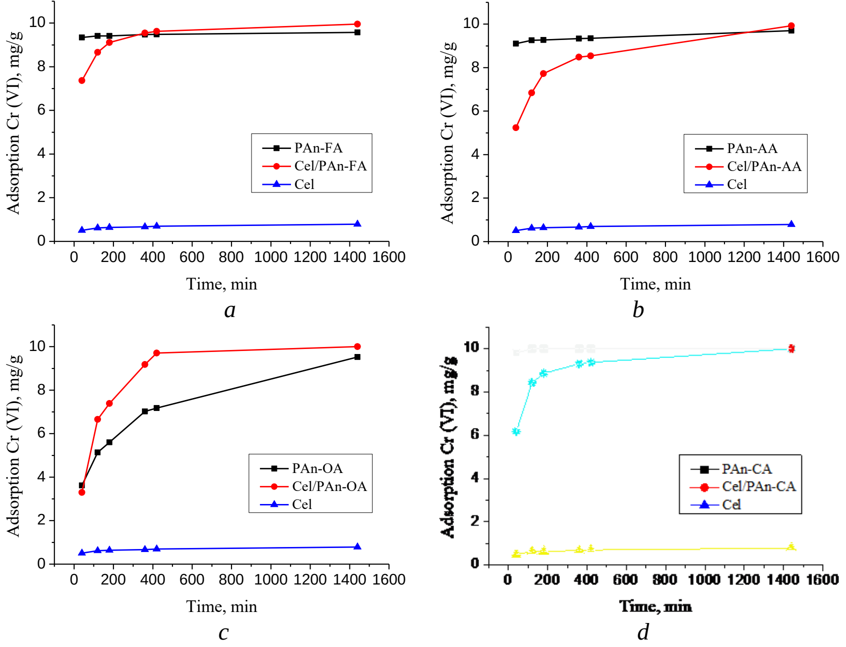
where: $A_{\max}$ – the maximum adsorption capacity of the adsorbent in relation to Cr(VI), mg/g; C_t – concentration of Cr(VI) at a specific time, mg/L; K_L – Langmuir constant, L/mg; K_F and $1/n_F$ are constants of the Freundlich isotherm, which are related to the adsorption capacity of the adsorbent, mg/g (mg/g)(L/mg)$^{1/n}$) and the intensity (favorability) of adsorption, respectively.

Equations (2) and (3) are linearized forms of the Langmuir and Freundlich adsorption isotherm equations, respectively, which are used to graphically establish the unknown parameters of these isotherms. The parameters obtained using various isotherm models are important for establishing the adsorption mechanisms, surface characteristics, and affinity of the components of the adsorption system.

3. Results and discussion

3.1. Kinetics of adsorption

The efficiency of Cr(VI) removal from model aqueous solutions by samples of PAn, Cel/PAn, synthesized in aqueous solutions of carboxylic acids, as well as Cel was considered in the paper [33]. The results of studying the kinetics of Cr(VI) adsorption at different initial concentrations by PAn samples and Cel/PAn composites, in which PAn was in a state doped with CXAs during the synthesis, are shown in Figs. 1–4. For comparison, the kinetic curves of Cr(VI) adsorption by the sample Tsel are given. We can see that the CXAs used for the synthesis of samples have different effects on the kinetics of adsorption of Cr(VI) oxyanions by these adsorbent samples. Analysis of the kinetic curves of Cr(VI) adsorption by PAn–FA, PAn–AA and PAn–CA samples from solutions with concentrations of 100 and 200 mg/L shows that the amount of adsorbed Cr(VI) in the first 20 min reaches almost maximum values (Figs. 1, *a*, *b*, *d* and 2, *a*, *b*, *d*).



a *b*

c *d*

Fig. 1. Kinetics of Cr(VI) adsorption from a solution with a concentration of 100 mg/L by samples:
a – PAn–FA, Cel/PAn–FA and Cel; *b* – PAn–AA, Cel/PAn–AA and Cel;
c – PAn–OA, Cel/PAn–OA and Cel; *d* – PAn–CA, Cel/PAn–CA and Cel

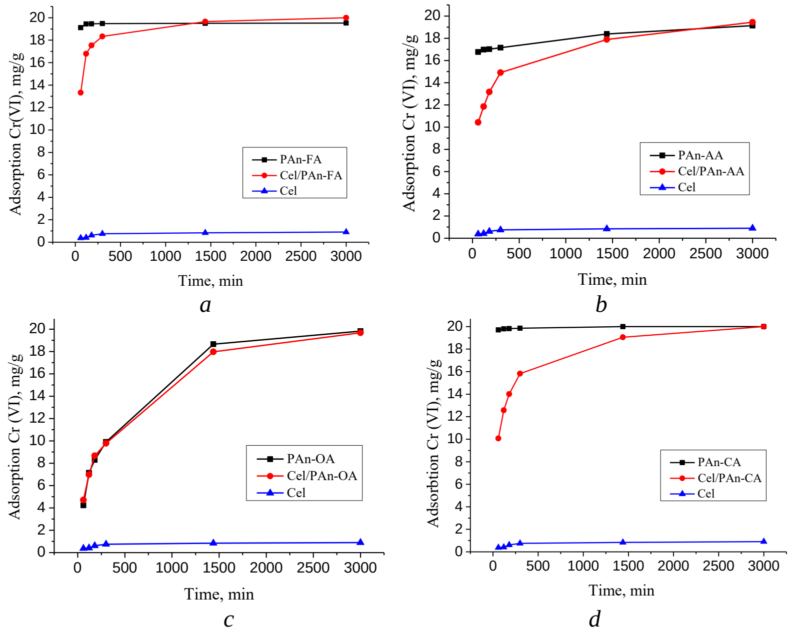


Fig. 2. Kinetics of Cr(VI) sorption from a solution with a concentration of 200 mg/L by samples: *a* – PAn–FA, Cel/PAn–FA and Cel; *b* – PAn–AA, Cel/PAn–AA and Cel; *c* – PAn–OA, Cel/PAn–OA and Cel; *d* – PAn–CA, Cel/PAn–CA and Cel

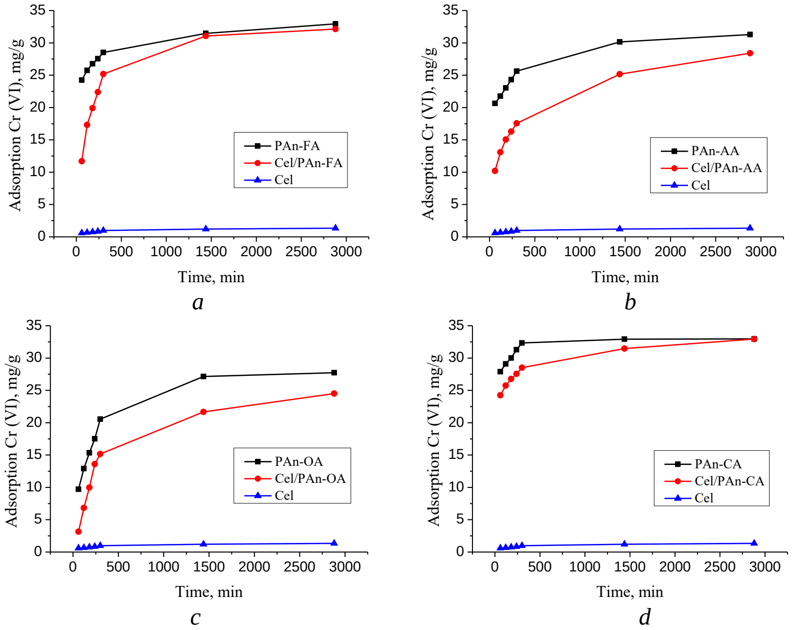


Fig. 3. Kinetics of Cr(VI) sorption from a solution with a concentration of 330 mg/L by samples: *a* – PAn–FA, Cel/PAn–FA and Cel; *b* – PAn–AA, Cel/PAn–AA and Cel; *c* – PAn–OA, Cel/PAn–OA and Cel; *d* – PAn–CA, Cel/PAn–CA and Cel

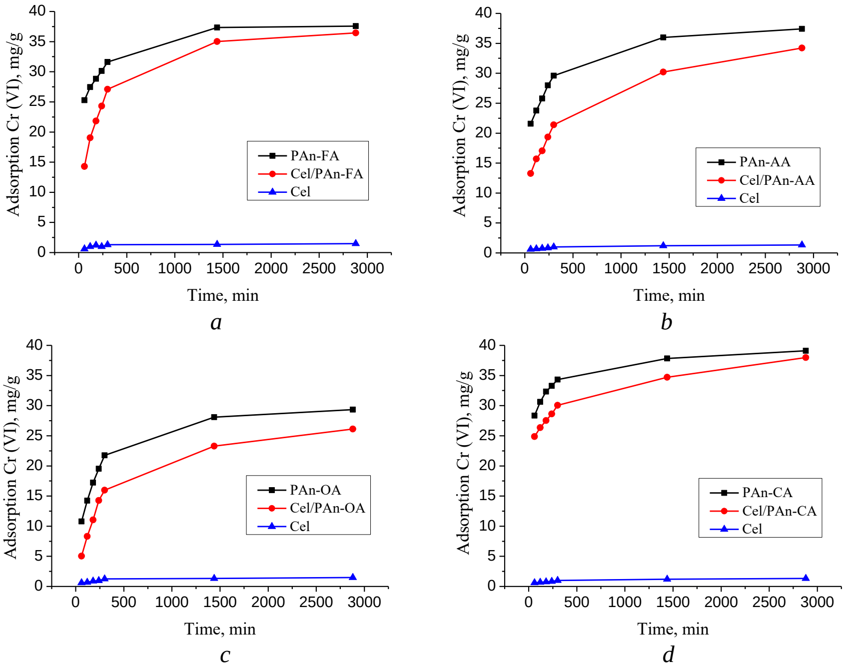
At concentrations of Cr(VI) in the initial solutions of 330 and 400 mg/L, the process of reaching the "plateau" of the kinetic curves is longer (Figs. 3, *a*, *b*, *d* and 4, *a*, *b*, *d*). The process of Cr(VI) adsorption by the PAn–OA sample at both low and higher concentrations of Cr(VI) is longer (Figs. 1, *c*, 2 *c*, 3 *c*, and 4, *c*), and the adsorption capacity of the PAn–OA sample is smaller.

Analysis of the kinetic curves of Cr(VI) adsorption by Cel/PAn samples from solutions with concentrations of 100 and 200 mg/L shows that the output of the curves to the "plateau" is longer (Figs. 1–4). According to the adsorption capacity values, the Cel/PAn samples practically coincide with the adsorption capacities of the PAn samples.

As can be seen from the kinetic dependences (Figs. 1, *a*, *b*, *d* and 2, *a*, *b*, *d*), adsorption of Cr(VI) from solutions with Cr(VI) concentrations of 100 and 200 mg/L by samples of PAn–FA, PAn–AA and PAn–CA is a fast one-step process. At Cr(VI) concentrations of 330 and 400 mg/L, a bend can be traced in the kinetic curves, which practically means a two-stage adsorption process (Figs. 3, *a*, *b*, *d* and 4, *a*, *b*, *d*).

The highest values of the adsorption capacity are illustrated by the Cel/PAn–CA samples (Figs. 1, *g*, 2, *g*, 3, *g*, 4, *g*). PAn–OA samples and Cel/PAn–OA samples show the lowest adsorption capacity (Figs. 1, *c*, 2, *c*, 3, *c*, 4, *c*).

At Cr(VI) concentrations of 330 and 400 mg/L, reaching the maximum adsorption capacity by Cel/PAn samples is slower than by PAn samples. The lower rate of adsorption by the Cel/PAn samples is obviously caused by the greater porosity of the PAn layers deposited on the surface of the Cel microfibrils.



a *b*

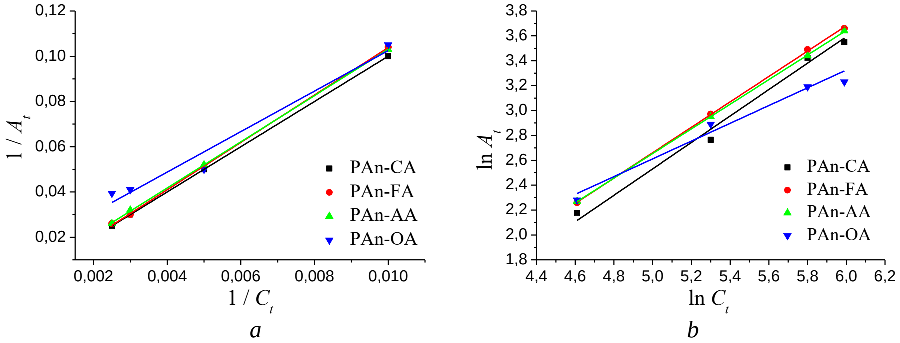
c *d*

Fig. 4. Kinetics of Cr(VI) sorption from a solution with a concentration of 400 mg/L by samples:
a – PAn–FA, Cel/PAn–FA and Cel; *b* – PAn–AA, Cel/PAn–AA and Cel;
c – PAn–OA, Cel/PAn–OA and Cel; *d* – PAn–CA, Cel/PAn–CA and Cel

Adsorption of Cr(VI) by the Cel sample is insignificant and does not depend on the concentration of the initial solutions (Figs. 1–4).

3.2 Adsorption isotherms of Cr(VI) by samples of PAn and Cel/PAn composites

The adsorption isotherms of Cr(VI) by PAn-carboxylic acid samples, constructed according to the linearized forms of the Langmuir and Freundlich isotherm equations (equation 2 and 3), are shown in Fig. 5.



a *b*

Fig. 5. Isotherms: *a* – Langmuir; *b* – Freundlich for adsorption of Cr(VI) by PAn-carboxylic acid samples

The values of the parameters of the adsorption isotherms, obtained from the corresponding graphic dependencies, are recorded in the Table 1. From Fig. 5 shows that all the isotherms are practically linear dependencies, i.e., the Langmuir and Freundlich models describe Cr(VI) adsorption by PAn samples and Cel/PAn composites well. The values of correlation coefficients (R^2) of these isotherms are also high (Table 1). However, the R^2 values for the Freundlich isotherm are somewhat smaller.

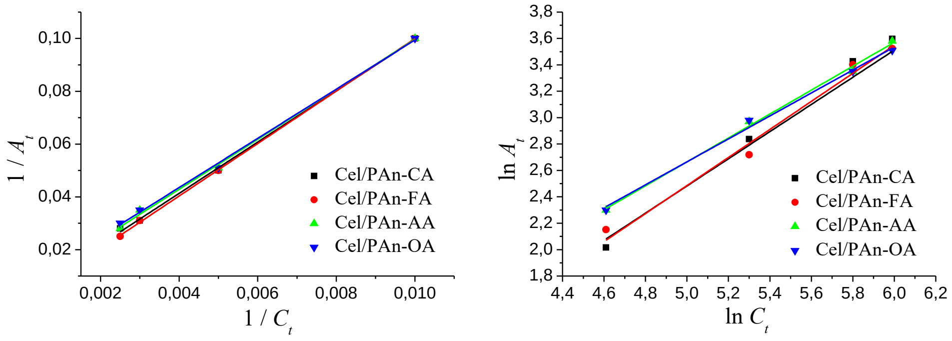
This proves that the Langmuir model is better suited for the description of Cr(VI) adsorption by PAn samples than the Freundlich model. Also, this may indicate that on the surface of the adsorbents there are energetically equivalent adsorption centers on which monolayer adsorption of Cr(VI) occurs.

Table 1

Values of Langmuir and Freundlich isotherm parameters for Cr(VI) adsorption on PAn-carboxylic acid samples

Adsorption isotherm model	Sample	R^2	A_{max}, mg/g	K_L, L/mg	K_F, mg/g	$1/n_F$
Langmuir	PAn–FA	0.9998	106.42	$8.97 \cdot 10^{-5}$	–	–
	PAn–AA	0.9998	110.76	$8.89 \cdot 10^{-5}$	–	–
	PAn–OA	0.9767	77.16	$4.45 \cdot 10^{-5}$	–	–
	PAn–CA	1.0000	115.28	$11.22 \cdot 10^{-5}$	–	–
Freundlich	PAn–FA	0.9986	–	–	0.0868	0.9809
	PAn–AA	0.9988	–	–	0.1009	0.9896
	PAn–OA	0.9694	–	–	0.3836	0.8139
	PAn–CA	0.9835	–	–	0.6191	1.0000

Cr(VI) adsorption isotherms by Cel/PAn samples are shown in Fig. 6. The values of the parameters of the adsorption isotherms, obtained from the corresponding graphic dependencies, are recorded in the Table 2.



a *b*

Fig. 6. Isotherms: *a* – Langmuir; *b* – Freundlich for adsorption of Cr(VI) by Cel/PAn–carboxylic acid samples

From Fig. 6 and it can be seen that all the isotherms are practically linear, that is, the Langmuir and Freundlich models describe Cr(VI) adsorption by Cel/PAn samples well. The values of correlation coefficients (R^2) of Langmuir isotherms are greater compared to R^2 of Freundlich isotherms (Table 2).

The $A_{\max}$ values obtained from the Langmuir isotherms are the so-called theoretical values and for the studied adsorbents PAn-carboxylic acid and Cel/PAn-carboxylic acid are sufficiently high values (Tables 1 and 2).

Table 2

Values of Langmuir and Freundlich isotherm parameters for Cr(VI) adsorption on Cel/PAn–carboxylic acid samples

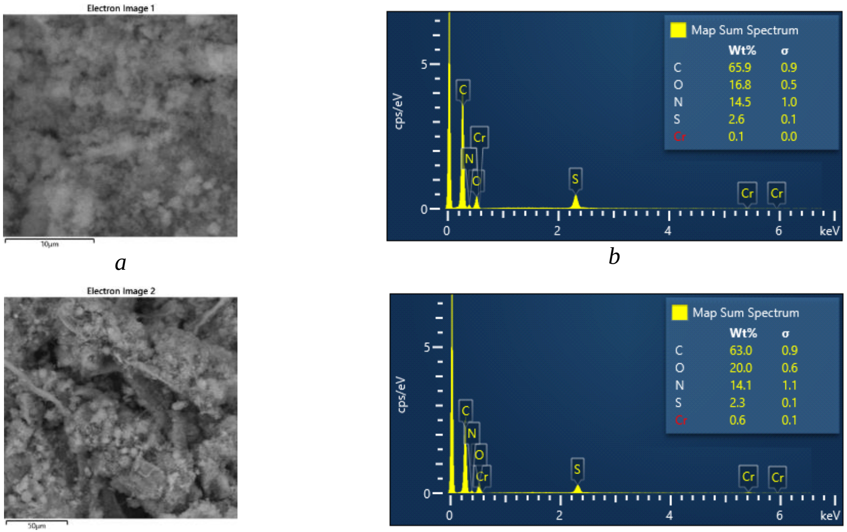
Adsorption isotherm model	Sample	R^2	A_{max}, mg/g	K_L, L/mg	K_F, mg/g	$1/n_F$
Langmuir	Cel/PAn–FA	0.9997	188.73	$5.63 \cdot 10^{-4}$	–	–
	Cel/PAn–AA	0.9977	201.61	$5.24 \cdot 10^{-4}$	–	–
	Cel/PAn–OA	0.9978	160.51	$3.68 \cdot 10^{-4}$	–	–
	Cel/PAn–CA	0.9985	206.50	$5.53 \cdot 10^{-4}$	–	–
Freundlich	Cel/PAn–FA	0.8923	–	–	0.1590	1.0630
	Cel/PAn–AA	0.9549	–	–	0.1544	0.9066
	Cel/PAn–OA	0.9632	–	–	0.1847	0.8708
	Cel/PAn–CA	0.9899	–	–	0.0994	1.0300

The Langmuir isotherm model assumes the existence of a monolayer coating of the adsorbent surface with an adsorbate, and adsorption occurs on a certain energetically homogeneous surface. The Freundlich adsorption isotherm model is empirical and more general than the Langmuir model, and considers the energetic heterogeneity of the surface [35].

3.3. SEM–EDX analysis of adsorbent samples after adsorption

In Fig. 7 shows, as an example, the results of the study, namely, the SEM-image, EDX-spectrum, and elemental maps of the PAn-FA and Cel/PAn-FA sample after adsorption of Cr(VI) oxyanions from an aqueous solution with a concentration of 100 mg/L. As we can see from Fig. 7, *b*, *d*, in addition to the elements carbon (C), oxygen (O) and nitrogen (N), as the main components of the sample Cel/PAn–CA, there is adsorbed chromium (Cr) and a certain amount of sulfur (S).

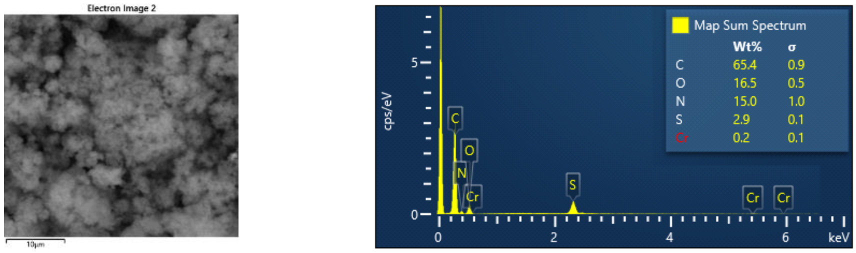
As we can see from Fig. 8, *a*, the morphology of polyaniline particles of the PAn–CA sample is similar to the morphology of the PAn–FA sample. The Cel/PAn–CA sample is studied in more detail due to the peculiarity of the citric acid structure.



a *b*

c *d*

Fig. 7. SEM-image (*a*) and EDX-spectrum (*b*) of the PAn-FA, and SEM-image (*c*), and EDX-spectrum (*d*) of the Cel/PAn-FA samples after Cr(VI) adsorption



a *b*

Fig. 8. SEM-image (*a*) and EDX-spectrum (*b*) of the PAn–CA sample after Cr(VI) adsorption

In Fig. 9 shows the results of the SEM-EDX study, namely the SEM-image, EDX- spectrum, and elemental maps of the Cel/PAn–CA sample after adsorption of Cr(VI) oxyanions from an aqueous solution with a concentration of 100 mg/L.

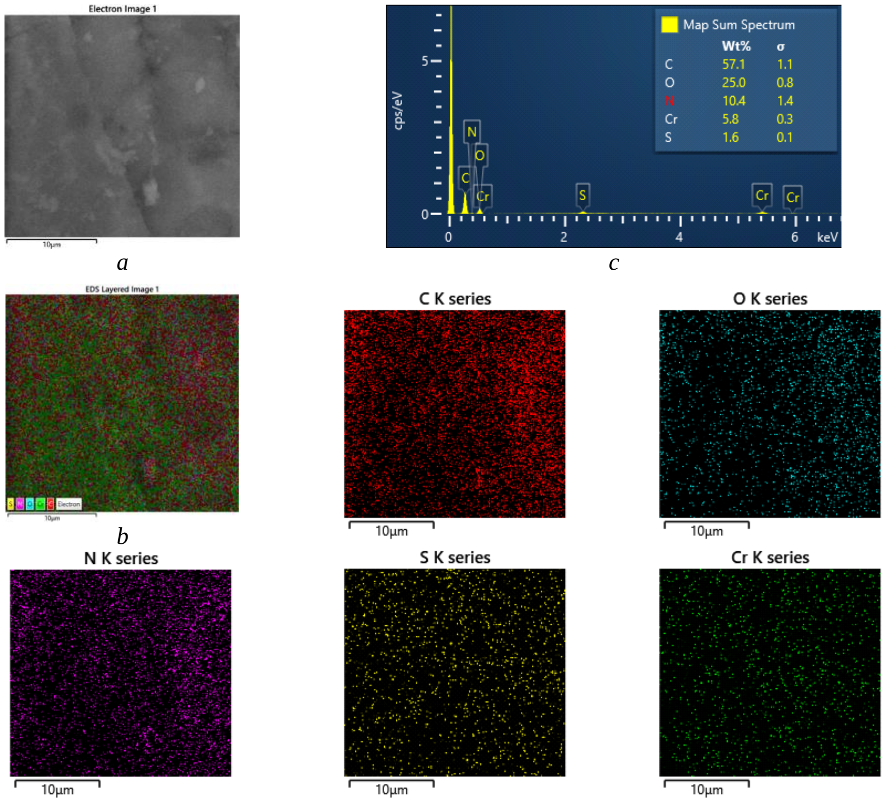


Fig. 9. SEM-image (*a*); summary elemental maps (*b*); EDX-spectrum (*c*); elemental maps (*d*) of the Cel/PAn–CA sample after Cr(VI) adsorption

In Fig. 9, *a* shows the surface of a cellulose microfibril covered with a thin layer of polyaniline. As we can see from Fig. 9, *c*, in addition to the elements carbon (C), oxygen (O) and nitrogen (N), adsorbed chromium (Cr) is present. The Cr content is 5.8±0.3 %, which is a sufficiently high value. The elemental maps (see Fig. 9, *d*) show an almost uniform distribution of elements on the surface of the cellulose microfibril coated with polyaniline.

The presence of chromium in adsorbent samples after removal of Cr(VI) from aqueous solutions was also confirmed by X-ray fluorescence analysis [31]. Based on the presence of Cr on the adsorbent samples and the absence of Cr(VI) oxyanion in the solution after adsorption [31], as well as the analysis of the results of works [19, 37], it can be concluded that the adsorbed Cr(VI) oxyanion on PAn and Cel/PAn samples is completely is reduced by polyaniline to Cr(III).

Synthesized composite materials based on cellulose and polyanilines doped with formic and citric acids in the synthesis process demonstrated good adsorption capacity for Cr(VI) oxyanions from solutions with concentrations of 100–400 mg/L. The adsorption process mainly corresponds to the Langmuir adsorption isotherm, which indicates that the adsorption is of a chemical nature. The values of the correlation coefficient of the parameters of the Freundlich isotherm are close to the values characteristic of the Langmuir isotherm. This proves that the dominant chemical adsorption is closely related to physical adsorption, which precedes the course of chemical adsorption. It is obvious that, based on the kinetic curves, it is possible to claim that the course of physical and chemical adsorption is practically parallel

Future research is needed into aspects of influencing factors, including the choice of dopant acid, aniline : cellulose ratio, reusability of materials, etc., to evaluate the potential ability of these materials in a wider application for the purification of waters of various origins from Cr(VI) oxyanions.

4. Conclusions

Samples of polyaniline and cellulose/polyaniline composites, in which polyaniline was doped in the synthesis process with carboxylic (formic, acetic, oxalic, and citric) acids, were used to study adsorption from model aqueous solutions of Cr(VI) without additional acidification of the adsorbent solutions.

As a result of studies of the suitability of the synthesized samples for the adsorption of Cr(VI) ions, it was found that the Cel/PAn–FA and Cel/PAn–CA composites are the most effective sorbents for the removal of Cr(VI) oxyanions. Also, the research results showed that the adsorption of Cr(VI) on the Cel/PAn-carboxylic acid composites is better described by the Langmuir isotherm, since the values of the correlation coefficients are quite high ($R^2 \approx 0.9976$).

A comparison of the adsorption capacities of PAn samples and samples of Cel/PAn composites shows that approximately twice the mass of polyaniline in the composite samples adsorbs the same amount of Cr(VI) oxyanions.

Optimizing the synthesis conditions and especially the cellulose/polyaniline ratio can lead to even better results of the adsorption capacity of composites created on the basis of cellulose and polyaniline.

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АДСОРБЦІЯ Cr(VI) ПОЛІАНІЛІНАМИ ТА КОМПОЗИТАМИ ЦЕЛЮЛОЗА/ПОЛІАНІЛІН, СИНТЕЗОВАНИМИ У ВОДНИХ РОЗЧИНАХ КАРБОНОВИХ КИСЛОТ

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Зразки поліаніну (ПАн) та композитів целюлоза/поліанілін (Цел/ПАн), отримані окиснювальною полімеризацією аніліну у водних 0,5 М розчинах карбонових (форміатна, ацетатна, оксалатна та цитратна), використано для дослідження адсорбції Cr(VI) із модельних водних розчинів. Співвідношення анілін : целюлоза за синтезу композитів Цел/ПАн становило 1 : 1 (г : г). Поліанілін як у зразках ПАн, так і в зразках Цел/ПАн після синтезу перебував у допованій карбоновими кислотами формі.

За результатами адсорбційних досліджень побудовано кінетичні криві адсорбції Cr(VI) із водних розчинів з концентраціями 100, 200, 330 та 400 мг/л зразками ПАн та зразками композитів Цел/ПАн. Дослідження кінетики адсорбції зразками ПАн із розчинів з концентраціями Cr(VI) 100 та 200 мг/л показало, що процес є одностадійним, а за концентрацій 330–400 мг/л − двостадійним. Адсорбція Cr(VI) з розчинів з концентраціями 100, 200, 330 та 400 мг/л зразками Цел/ПАн є двостадійним процесом. Адсорбційна ємність як зразків ПАн, так і композитів Цел/ПАн залежить від концентрації Cr(VI) у вихідних розчинах. Збільшення початкової концентрації Cr(VI) у розчинах приводить до збільшення значень величин адсорбції як на першій стадії, так і на другій стадії процесу зразками ПАн і зразками Цел/ПАн. Перебіг другої стадії процесу адсорбції, яка, очевидно, включає і сорбцію, є тривалішим, проте саме під час неї досягаються практично максимальні значення адсорбційних ємностей стосовно Cr(VI). Причому додаткові дослідження показали, що адсорбційна ємність поліанілінів у зразках композитів Цел/ПАн (тобто без урахування маси целюлози) досягає величин у приблизно два рази більших за адсорбційну ємність зразків поліанілінів.

За результатами досліджень побудовано ізотерми Ленгмюра та Фрейндліха. З’ясовано, що процес адсорбції Cr(VI) зразками ПАн та Цел/ПАн, у яких ПАн, допований різними органічними кислотами, найкраще узгоджується з адсорбційною моделлю Ленгмюра.

Ключові слова: поліаніліни, композити, целюлоза/поліанілін, карбонові кислоти, адсорбція, хром(VI).

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