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COMPARATIVE ANALYSIS OF ABSORPTION CAPACITY OF CR(VI) POLYANILINE AND CELLULOSE/POLYANILINE COMPOSITES SYNTHESIZED IN AQUEOUS SOLUTIONS OF ORGANIC ACIDS

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Samples of polyaniline (PAn) doped by different organic acids, namely PAn-FA, PAn-AA, PAn-OA, and PAn-CA, were synthesized by oxidation of aniline (An) with ammonium peroxydisulfate in the 0.5 M aqueous solutions of formic (FA), acetic (AC), oxalic (OA), and citric acids (CA) respectively. Samples of composites of cellulose (Cel) with doped polyaniline (Cel/PAn-FA, Cel/PAn-AA, Cel/PAn-OA, and Cel/PAn-CA)were produced by same method under the presence of a suspension of microfibrillar bleached cellulose in the reaction mixture. The mass ratio of An : Cel was 1 : 1. The structure of obtained samples was studied using X-ray diffraction, FTIR spectral analysis, and scanning electron microscopy.

Adsorption capacity as concerns Cr(VI) by produced samples of both individual polyanilines and composites and adsorption kinetics has been studied by electronic (UV) and fluorescence X-ray spectroscopy and also X-ray energy dispersion analysis methods. Practically full removal of Cr(VI) ions (98–100 %) of such investigated samples of PAns and its composites has been determined.

The adsorption kinetics is good described by equations of pseudo first and second orders. According to the results, the Langmuir and Freundlich adsorption isotherms are plotted. It was found that the process of adsorption Cr(VI) ions by doped samples of PAn and Cel/PAn accords to adsorption model of Langmuir. It has been shown, that adsorbed chromium remains in the samples of adsorbents in the form of chromium (III).

Keywords: polyaniline, cellulose, composites, structure, Cr(VI), adsorption.

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1. Introduction

Polyaniline (PAn) is one of the most abundant polymers of new class of materials-electrically conductive polymers (ECPs). Due to its numerous and unique physicochemical properties, such as catalytic and adsorption properties, takes the significant interest of researchers in PAn, as can be seen in many publications [1–3].

Over the last few decades, the possibilities of applications of ECP and PAn have been actively studied, especially for various processes and technologies [4–12].

On the one side, wide range of important physicochemical properties, such as unique orderliness of the structure [3] and large diversity of morphology of polyaniline particles [13], propel of its attractiveness for investigations [1–12]. Under certain conditions, polyaniline possess the largest number of forms-states [3–7] that is important property and distinguishes it from another ECP. Fast transforming (switching) of PAn from one state-form to another is used for creation of various devices in modern technologies [1–12]. On the other side, PAn is a brittle-powdery polymer, therefore in many cases it is applied on various inorganic [14] and organic polymeric nature [15] matrices-carriers. Polyaniline combines in these composites excellent due to its high affinity for the surfaces of different materials and strong hydrophilicity. Different types of cellulose are successfully used to build such carrier matrices of PAn [16–21]. Cellulose is most abundant, and an important renewable biopolymer found in the nature. The worldwide biomass production of cellulose is target more than 1,5 trillion tons yearly [22]. Cellulose has such essential properties as hydrophilicity, biocompatibility, and biodegradation. In addition, cellulose is insoluble in water and common organic solvents due to its high crystallinity. It is well known that Cel is a fibrous biopolymer and suitable to build a variety of composites with ECPc, caused by high similarity of chemical as well as mechanical properties [15–23]. Cellulose is characterized high hydrophilicity and chemical resistance to treatment by variety of acids [23]. These attitudes are an important factor for synthesis of composites with ECPs and PAn [15–22]. The main goal is to research the opportunities of combining electrically conductive and redox properties of PAn with specific chemical and physical characterizations of Cel, namely high mechanical strength and chemical resistance in different environments with purpose to bring variety of hybrid composites being [15–20, 24–27].

Heavy metals are one of the secondary products of progressing global industrialization, consequently what is one of the most dangerous pollutants in water and food. Due to their ability to accumulate and high toxicity in organisms, they are causing vitally risks to human health [28–29]. Mental and neurological disorder can be caused by accumulation of transported and exposed heavy metals, such as mercury, plumbum, arsenic, cadmium, chromium, and others. Chromium is classified as a carcinogenic substance, that ranks 5th among toxic elements [30–32].

Chromium is geochemical element that is common in rocks, soils, mineral clays, waters and the atmosphere [29]. Natural reservoirs are polluted due to domination of variety of technological processes of chromium-containing ores [33]. The total Cr concentration in spring and sea waters varies between 0.11–117 mg/L and 0.21–50 mg/L [28]. Chromium exists as oxyanion in aqueous solutions with oxidation states +3 (Cr(III)) and +6 (Cr(VI)). The presence and ratio of these two states depend on chemical and photochemical redox transformation, release into atmosphere/dissolution, and reactions of adsorption/desorption on natural objects [34]. There are also significant anthropogenic

sources of chromium in galvanic, electronic, metallurgical, leather, wood preservatives, and textile industries. As usual, Cr(VI) in total concentrations up to $100 \, mg \cdot L^{-1}$ is found in industrial wastewater [35]. Moreover, it should be noted that processing industry of leather is one of the biggest chromium polluters of environment [36]. Whereas its high toxicity and hazardous impact on environment, the pollution of Cr(VI) in wastewater has been strictly controlled for a long time [28–29] by environmental legislation of many countries and should not exceed 0.1 mg/L [37].

However, chromium is an important chemical element that the human body requires to function. For example, chromium is an essential nutrient required for sugar metabolism. This means that our body requires it when we eat sweets. On the contrary, with lack of chromium you want a sweet … vicious circle.

Hexavalent chromium presents in various oxoanionic forms, depending on pH of the aqueous solution and total concentration of Cr(VI), such as chromate, dichromate, and hydro chromate [38]. In a concentration range of 0.05–300 mg/L of Cr(VI) following types of particles are dominant: at $pH < 1$ $H_2CrO_4^-$, at pH 1–6.5 $HCrO_4^-$; at $pH > 6.5$ $Cr_2O_4^{2-}$ and CrO_4^{2-}. Oxoanionic form $Cr_2O_4^{2-}$ dominates at concentrations above 300 mg/L Cr(VI) and at pH 1–6.5 [39]. The relative amount of each type of oxoanionic forms of Cr(VI) is strongly related to the pH of solutions [38] as well as the pH of natural waters [39]. Several certified technologies are used to exclude Cr(VI) from aqueous solutions, namely, precipitation, reverse osmosis, ion exchange, variety of filtration, solvent extraction, chemical reduction/oxidation, electrochemical precipitation, and others [33, 35, 41]. However, all these methods have pros and cons or special limitations, including incomplete removal of metal, high consumption of reagent and used energy, low selectivity, formation of secondary waste and difficulty of its utilization [42, 43].

The combining properties of PAn and Cel are extremely useful for utilization of chromium compounds [33–47]. This combination is carried out by chemical oxidation of aniline by various oxidants, mainly in aqueous solutions of different acids in the presence of dispersed cellulose [15–20, 22–26, 44]. During the synthesis are formed acid-doped polyaniline layers on the surface of micro- and nanofibrils of cellulose. The composites obtained in this way by the in-situ method have great practical importance. Thus, the ways to combine the properties of cellulose and PAn are greatly simplified. Thereby resulting new materials with interesting physicochemical properties [45]. The macromolecules of cellulose consist of plenty hydroxyl groups, that can provide for grafting by various polymers on active side chains. The hydroxyl groups can act both as donors of electrons for reduction of hexavalent chromium, and as active centers for the deposition and retention of trivalent chromium [45]. The efficiency of deposition of PAn on the surface of Cel depends on reaction conditions for oxidation of aniline, nature of dopant acid, nature of oxidant, concentrations ratio as well as mass ratio of monomer/oxidant and monomer/cellulose, temperature of the synthesis, degree of dispersion and preliminary surface preparation of Cel. The application of different carboxylic acids as dopants can enhance the chemical affinity of the components in composites of Cel/PAn. In this study were synthesized and characterized properties of PAn composites with micro fibrillated Cel in solutions of formic, acetic, oxalic, and citric acids. Furthermore, sorption and structural properties related to compounds of Cr(VI) were investigated. Composite materials based on cellulose with polyaniline, doped with carboxylic acids are attractive for research to its environment-friendly and high specific strength properties.

An interesting aspect for utilization of these composites is that adsorption studies of Cr(VI) were performed at pH ~5.0–6.0, caused by dopant acid during the synthesis.

2. Experimental section
Reactants and materials
The composites of cellulose/polyaniline (Cel/PAn) were synthesized by chemical oxidation of aniline using ammonium peroxodisulphate $(NH_4)_2S_2O_8$ (APS), Aldrich, formic, acetic, oxalic, citric acids 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 1290 μm, viscosity 24700 mPa·s 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. Distilled water was used as solvent.

Synthesis of 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. Drop wise 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. All samples were dried in a vacuum oven at 50 ℃ for 24 h [45].

Synthesis of composites Cel/PAn
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 (FA), acetic (AA), oxalic (OA), or citric (CA) acid and simultaneously a sample of APS (2.67 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 with mechanical stirrer, following the solution of APS was added drop wise over the second hour and finally stirred for one hour. Composites were washed and isolated as PAn [48].

Preparation for investigation
The synthesized samples were dried in a vacuum oven at 50 ℃ and liquefied by 0.9 кG·cm^{-2}, after that pulverized 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.

Investigation of properties
Diffractograms of samples PAn and Cel/PAn were recorded on a diffractometer DRON-4-07 (radiation Cu Kα, λ=1.54060 Å). FTIR ATR spectra was performed using NICOLET IS 10 ATR spectrophotometer in the range of 4000–650 см$^{-1}$ with a step of scanning 5 см$^{-1}$.

The electrical conductivity of tableted samples was determined by method [49]. Rigol DM 3068 was employed to determine the electrical resistance of tablets, so 10 measurements have been done.

Morphology of the prepared PAn-CA and Gl/PAn-CA samples was studied using a ZEISS EVO 40XVP scanning electron microscope (SEM). All the SEM images were obtained by recording of the secondary electrons (SEs). The excitation of secondary radiation was achieved by irradiation of the samples by electrons beam with energy of 8 keV. A SMARTSEM software package was used for the SEM image analysis.

Chemical composition of the samples was determined via Energy Dispersive X-ray (EDX) spectroscopy using an INCA Energy 350 system. [50].

ElvaX PRO analyzer was employed for X-ray fluorescence analysis.

Investigation of adsorption

The adsorption of Cr(VI) was carried out under static conditions at at 20 ℃. To portion of adsorbent (PAn or composite of Cel/PAn) was added 10 ml (100 or 200 or 330 or 400 ml) solution of $K_2Cr_2O_7$, then after fixed time, 500 mcl of samples were taken for injection in 2 ml cuvette. Furthermore, it is examined by spectrophotometric analysis. Calibration curve was employed to determine the amount of adsorbed compound.

The adsorption of Cr (VI) in (%) from the solution was calculated by the equation:

$$A\ (\%) = 100\ (C_0 - C_r)\ /\ C_0,\tag{1}$$

and the equilibrium of adsorption by the equation:

$$A_p = (C_0 - C_r)\ V\ /\ m,\tag{2}$$

where, A_r – is amount of adsorbed Cr(VI) at equilibrium (mg/g); C_o – initial concentration of Cr(VI) (mg/L); C_r – equilibrium concentration of Cr(VI) (mg/L); V – volume of solution, L; m – is the mass of the adsorbent, g.

3. Results and discussions

X-ray diffraction analysis

Diffractograms of samples PAn and Cel/PAn are shown in Fig. 1. The presence of wide angle of diffraction indicates the amorphous structure of the obtained polyaniline in the samples of PAn as well as Cel/PAn. One diffraction peak of medium intensity at $2\theta=22.8°$ is typical for Cel [51, 52]. Another two observed peaks at $2\theta=10.7°$ and $16,5°$ are less intense. Furthermore, it should be note, that higher peaks intensity at $2\theta=22.8°$ of Cel/PAn-FA, Cel/PAn-AA and Cel/PAn-CA may indicate thinner layering of PAn at the surfaces of micro-fibrillated Cel.
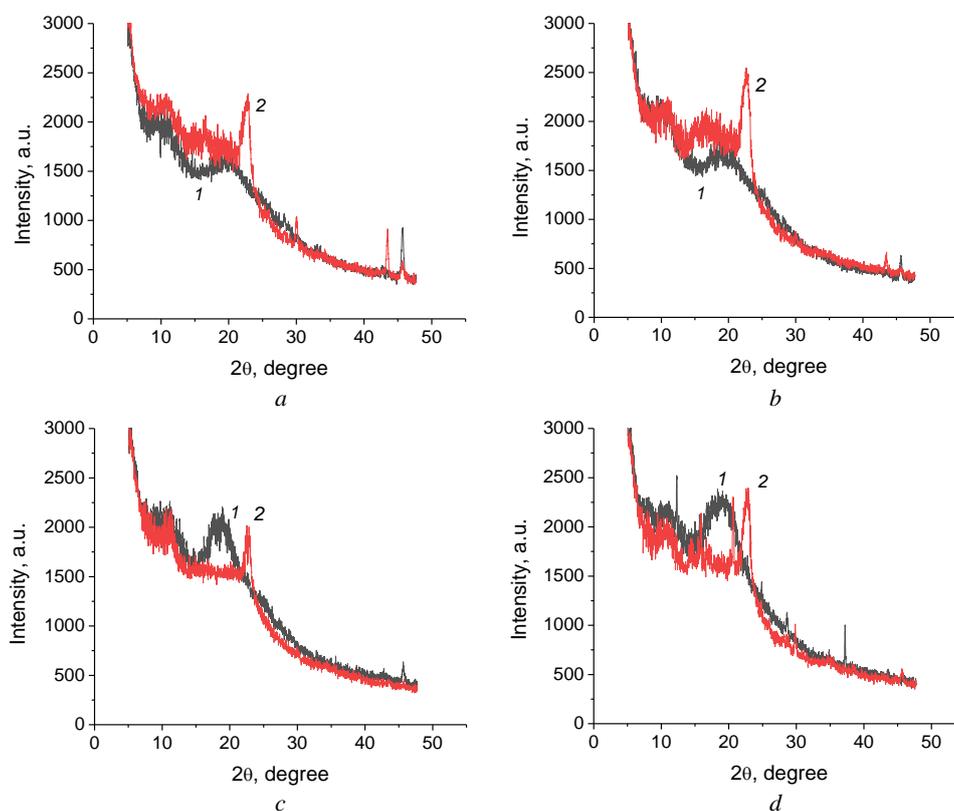
Fig. 1. X-ray diffraction spectra of samples, doped by different carboxylic acids: *a* − PAn-FA (*1*) and Cel/PAn-FA (*2*); *b* − PAn-AA (*1*) and Cel/PAn-AA (*2*); *c* − PAn-OA (*1*) and Cel/PAn-FA (*2*); *d* − PAn-CA (*1*) and Cel/PAn-CA (*2*)

FTIR-ATR Spectroscopy

FTIR spectra of samples of PAn and Cel/PAn, which were synthesized in aqueous solutions of various organic acids, as well as Cel, are shown in Fig. 2, are identical to spectra given in [18, 26, 43, 45, 49, 53, 54]. Polyaniline is identified by the characteristic bands, namely at 3245–3250 cm^{-1} (various intramolecular valence vibrations of N–H groups due to H-bonding) [49, 53−55], doublet of band at ~1577 cm^{-1} (valence oscillations of −C=C− in quinoid rings (*Q*)) and ~1475 cm^{-1} (benzenoid (*B*)), respectively, peak and shoulder at ~1300 and ~1240 cm^{-1} (C–N and C−N$^{+•}$ stretching and p-electron delocalization), these vibrations are indication of the protonated state of PAn and presence of its emeraldine salt [18, 19, 49, 52, 56] (see Table 1).

FTIR spectra of composites show similar characteristic peaks attributed to PAn, that indicate high-quality covered surface of micro-fibrillated Cel with layers of polyaniline. However, some characteristic peaks are slightly offset in different directions. According to FTIR spectra, the largest shift corresponds to composite of Cel/PAn-CA. It may be caused due to impact of dopant acid on the structure of macromolecular chains of PAn and strengthening of H-bonding between the functional groups of Cel and PAn.
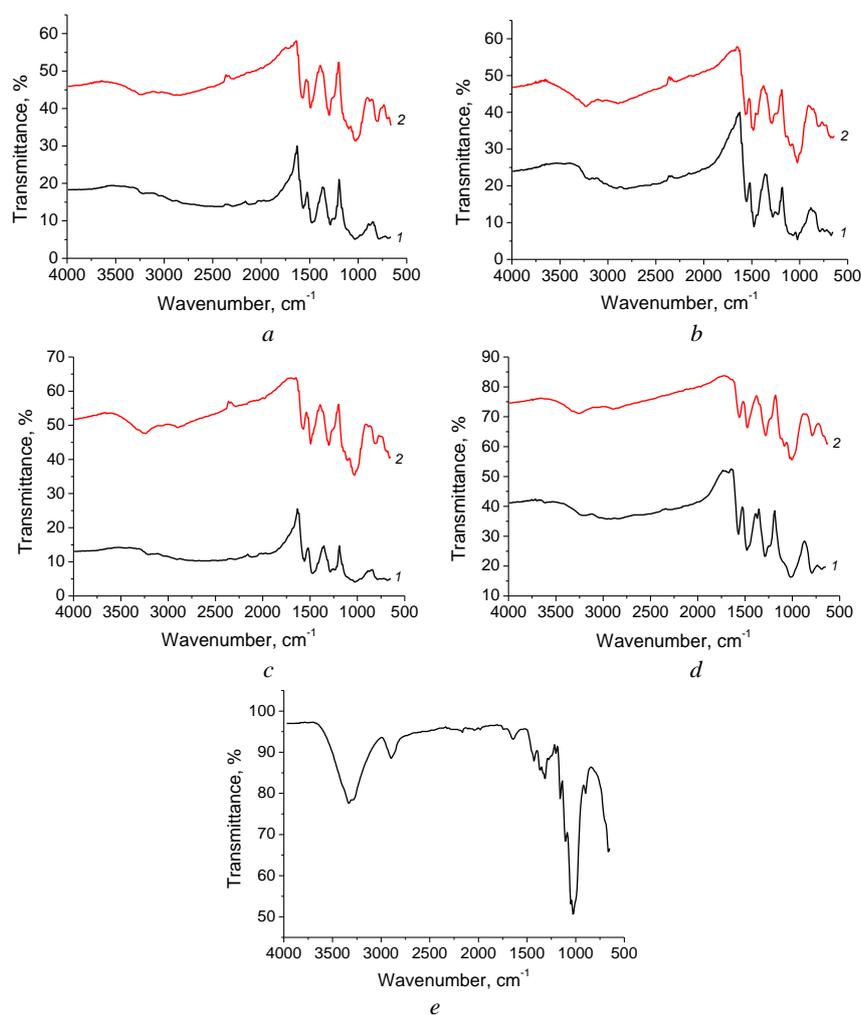
Fig. 2. FTIR-spectra of samples: *a* – PAn-FA and Cel/PAn-FA (curves *1* and *2*, respectively);
b – PAn-AA and Cel/PAn-AA (curves *1* and *2*, respectively); *c* – PAn-OA and Cel/PAn-OA (curves *1*
and *2*, respectively) *d* – PAn-CA and Cel/PAn-CA (curves *1* and *2*, respectively); *e* – Cel

Cellulose is identified by sharp characteristic bands at ~1 025 cm^{-1} (H- bonded valence vibrations C–O–C and H–O groups of cellulose) [26, 43, 53, 56]. Characteristic bands of cellulose and composites based on cellulose (see Fig. 2) are practically absent, except for strong peak at 1025 cm^{-1}, resulted electromagnetic shielded microfibers of Cel in the layer of PAn [17].

Despite the high content of Cel in composites (~50 %), the intensity of absorption of PAn exceeds the intensity of the signals of functional groups of Cel, particularly –O–H peaks at ~3440 cm^{-1}.

The absence of peak at ~3440 cm^{-1} endorsed strong interfacial H-bonded interaction at the surface of Cel between the macromolecules of PAn and Cel [45].

Characteristic peak at $1021.8 \, cm^{-1}$ of Cel is shifted towards larger values of wavenumbers, with an increase the number of carboxyl groups in dopant (at $1024.6 \, cm^{-1}$ for FA and AA as well as at $1032.9 \, cm^{-1}$ CA).

Table 1

FTIR-ATR Spectra. Characteristic wavenumbers of composites Cel/PAn-carboxylic acid and samples of PAn

Sample	Functional group wavenumbers*					
	$N{=}Q{=}N_e$	$N{-}B{-}N_e$	$C{-}N_e$	$C{-}N^{+\bullet}{}_e$	$C{-}N^{+}{}_e$	$C{-}H_{pp}$
	$\tilde{\nu} \pm 0.2$, cm^{-1}					
PAn-FA	1557.3	1475.3	1285.2	1235.2	1117.5	789.3
Cel/PAn-FA	1570.5	1491.2	1301.9	1239.0	1131.5	802.4
PAn-AA	1557.6	1484.6	1287.0	1232.6	1117.5	792.5
Cel/PAn-AA	1567.6	1494.4	1291.0	1232.6	1131.0	800.5
PAn-OA	1568.4	1485.8	1289.8	1239.5	1111.3	796.5
Cel/PAn-OA	1575.2	1495.1	1303.3	1247.6	1134.8	818.3
PAn-CA	1562.8	1477.4	1287.8	1239.7	1111.5	784.5
Cel/PAn-CA	1574.5	1488.2	1301.1	1237.4	1135.5	799.9

*Features: e – valence oscillation; p – plane of oscillation; pp – extraplanar oscillation; Q – quinoide ring oscillation; B – benzenoid ring oscillation.

The broad peak at about $3500{-}1750 \, cm^{-1}$ and shifted characteristic band of vibrations in benzenoid rings confirm the presence of H-bonding between PAn ($-N-B-N$), dopant-acid (C(O)OH) and micro-fibrils of cellulose ($-OH$) [26, 43, 53, 56]. Further the broad band at about $\sim 1200{-}900 \, cm^{-1}$ is associated with high degree of π-electron delocalization that can be achieved through the higher degree of oxidation of PAn [53]. Development and structural futures such composites are an important view of their implementation as adsorbents of hexavalent chromium from aqueous solutions.

Electrical conductivity of PAn and Cel/PAn samples

Specific conductivity (σ) of the synthesized samples have been measured to endorse the state form of PAn, as described in method [49]. The value of specific conductivity of the samples confirmed their state, doped with organic acids, as emeraldine form of doped PAn (see Table 2). As expected, the electrical conductivity of these samples is higher than the electrical conductivity of undoped composites.

As we can see from Table 2, PAn-FA has the highest specific electrical conductivity, followed by PAn-AA, PAn-CA and the lowest PAn-OA. The comparative decreases the electrical conductivity of composited to pure PAn is caused by dielectric properties of Cel, that prevent the flow of electrons. However, the results show, that PAn doped by carboxylic acids exist in the form of emeraldine salt. This determines the electrical conductivity of Pan [57]. Our results are comparative with the data of studies [44].

This study has shown, that Cel in composites of Cel/PAn doped by organic acids serves as a carrier matrix for macromolecules of PAn.

The removal of Cr(VI) from solutions using PAn and composites of Cel/PAn

The efficiency of removal of Cr(VI) from aqueous solutions various concentrations by PAn and composites of Cel/PAn, doped during the synthesis by carboxylic acids is illustrated in Fig. 3.
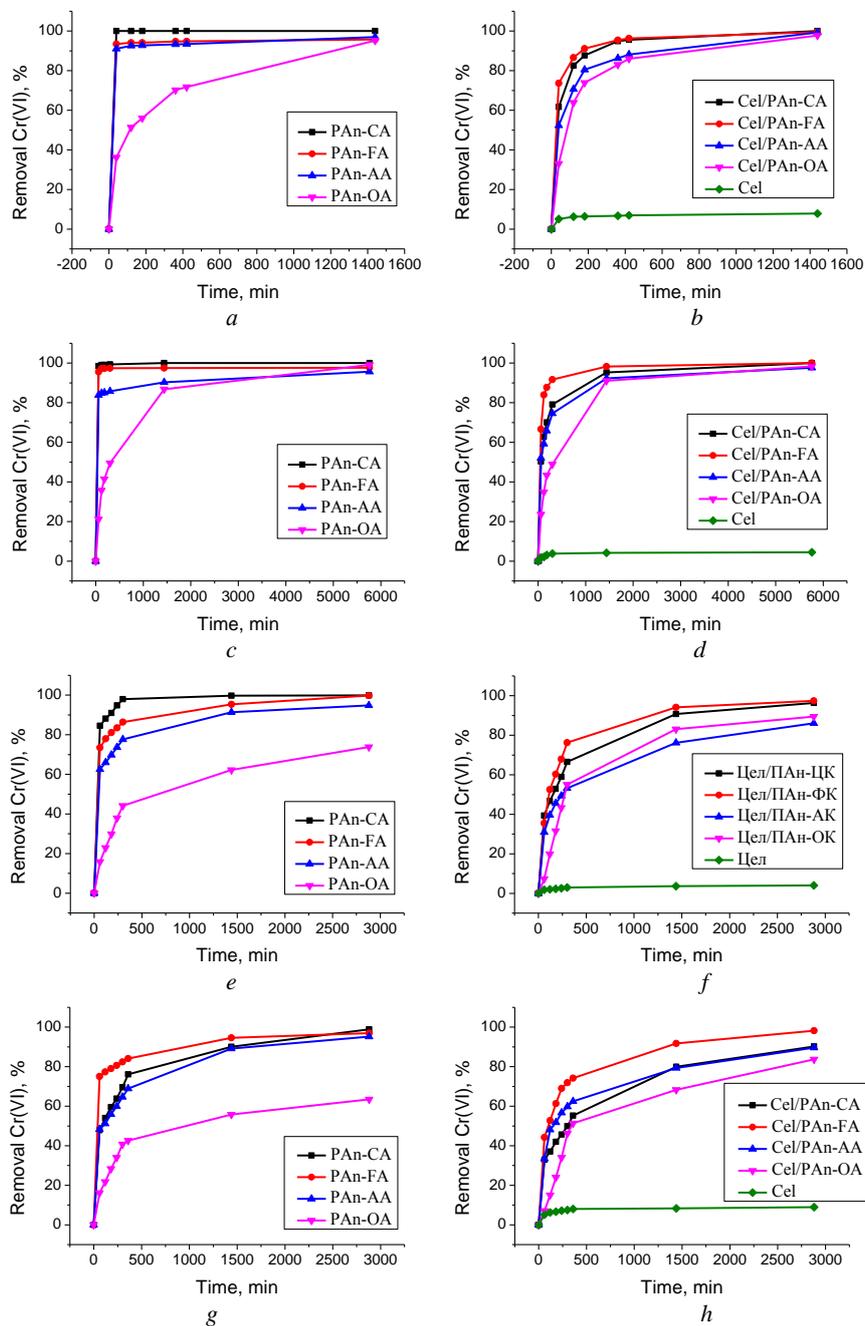
Fig. 3. Effect of the time of absorption on the percentage removal of Cr(VI) from solutions by
samples: *a, c, e, g* − PAn; *b*, *d*, *f*, *h* − Cel/PAn, doped by various acids.
Where, concentration of Cr (VI) in solution, mg/L: *a, b* − 100; *c*, *d* − 200; *e*, *f* − 330; *g*, *h* − 400

The initial concentrations of Cr(VI) solutions were 100, 200, 330, and 400 mg/L. The removal of Cr(VI), (in %) depends on the initial concentration of Cr(VI) in the solutions and time of contact with the investigated samples

As can been seen from Fig. 3, *a*, *c*, *e*, *g*, Cr(VI) ions have been completely adsorbed by macromolecules of PAn within 40 min. It is important to emphasize the slowest adsorption of Cr(VI) by the samples of PAn-OA. With increasing time of adsorption enhances the removal efficiency of hexavalent chromium. These graphs show absorption efficiency of investigated composites, as follows: 100 % absorption of Cr(VI)) by PAn-CA; 93.4 − PAn-FA; 91.1 − PAn-AA and 36.2 % − PAn-OA respectively. According to Fig. 3, the composite of PAn doped by citric acid is the best effective sorbent of Cr(VI). In contrast, adsorb samples of cellulose approximately 7−8 % of Cr(VI).
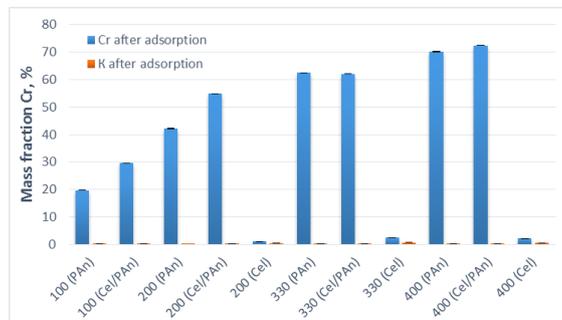
Interpretation of slope angle of kinetic curves in Fig. 3 leads us to the conclusion that the absorption rate of Cr(VI) by PAn at initial stage is higher, compared to slowly absorption of Cr(VI) by composites of Cel/PAn.

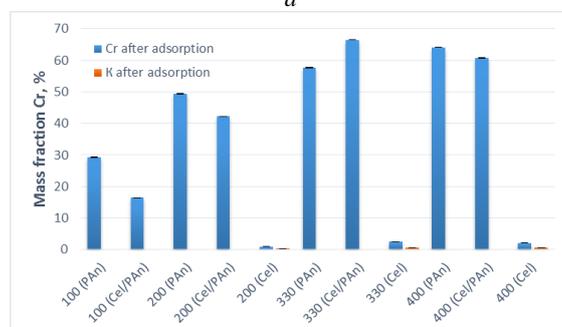*Elemental analysis of samples after adsorption of Cr(VI)*

We have employed X-ray fluorescence analysis to confirm the presence of adsorbed chromium in the samples of PAn and composites of Cel/PAn. Furthermore, quantitative determination of chromium in above mentioned samples has been studied. The results have been shown in the form of diagrams in Fig. 4.

As we can see from Fig. 4, chromium is present in all samples, which is mainly concentrated on the surface of PAn as well as Cel/PAn. Slight amounts of potassium were found in the adsorbent samples (see Fig. 4). Thus, for composites PAn-FA, Cel/PAn-FA and Cel/PAn-CA a clear pattern can be observed: composites of Cel/PAn adsorb Cr(VI) better from aqueous solutions than pure PAn (see Fig. 4, *a*, *d*). Slightly worse adsorption properties according to Cr(VI) are possessed composites of Cel/PAn doped by oxalic acid (see Fig. 4, *c*).
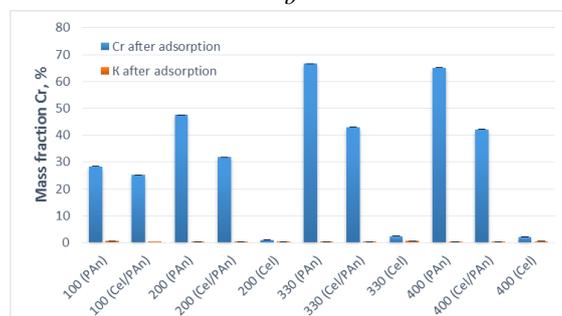
The higher mass fractions of adsorbed chromium on the surface of Cel/PAn-FA and Cel/PAn-CA composites in relation to the samples of PAn are caused by the larger surface area of polyaniline, deposited on the cellulose microfibrils. Given that the percentage of adsorption of Cr(VI) (see Fig. 3) and the content of adsorbed chromium by composites is quite high, it can be argued that the composites Cel/PAn-FA and Cel/PAn-CA are good adsorbents for removal Cr(VI) from aqueous solutions.
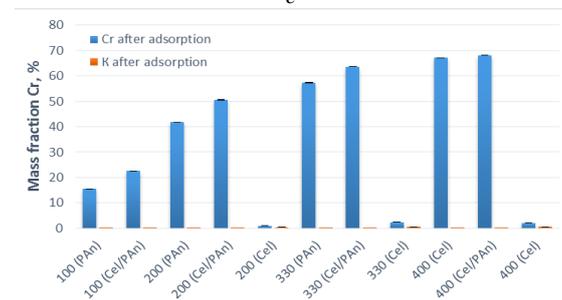
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a

b

c

d

Fig. 4. Content of chromium in powdered samples of PAn and composites of Cel/PAn,
doped by 0,5 M organic acids and Cel after adsorption.
Note: 100, 200, 330 and 400 – concentration of Cr(VI) in adsorbing solution at the beginning, mg/L

CEM analysis of samples after Cr(VI) adsorption

The SEM image of original sample of cellulose in Fig. 5, *a*, *b* and Fig. 5, *c*, as an example samples of PAn and Cel/PAn, which were synthesized in solutions of FA and CA after adsorption of Cr(VI); are shown. As we can see, cellulose microfibrils have a flat shape with different thickness, width and length. Especially, the rough surface of microfibrils can serve as a kind of matrix for the formation of layers of PAn. Samples of PAn (see Fig. 5, *c*, *e*), obtained in aqueous solutions of formic, acetic and oxalic acids are characterized by dispersed state with a highly developed surface [47]. Due to the properties of CA is the synthesized in aqueous citric acid solution sample of PAn more aggregated [58].
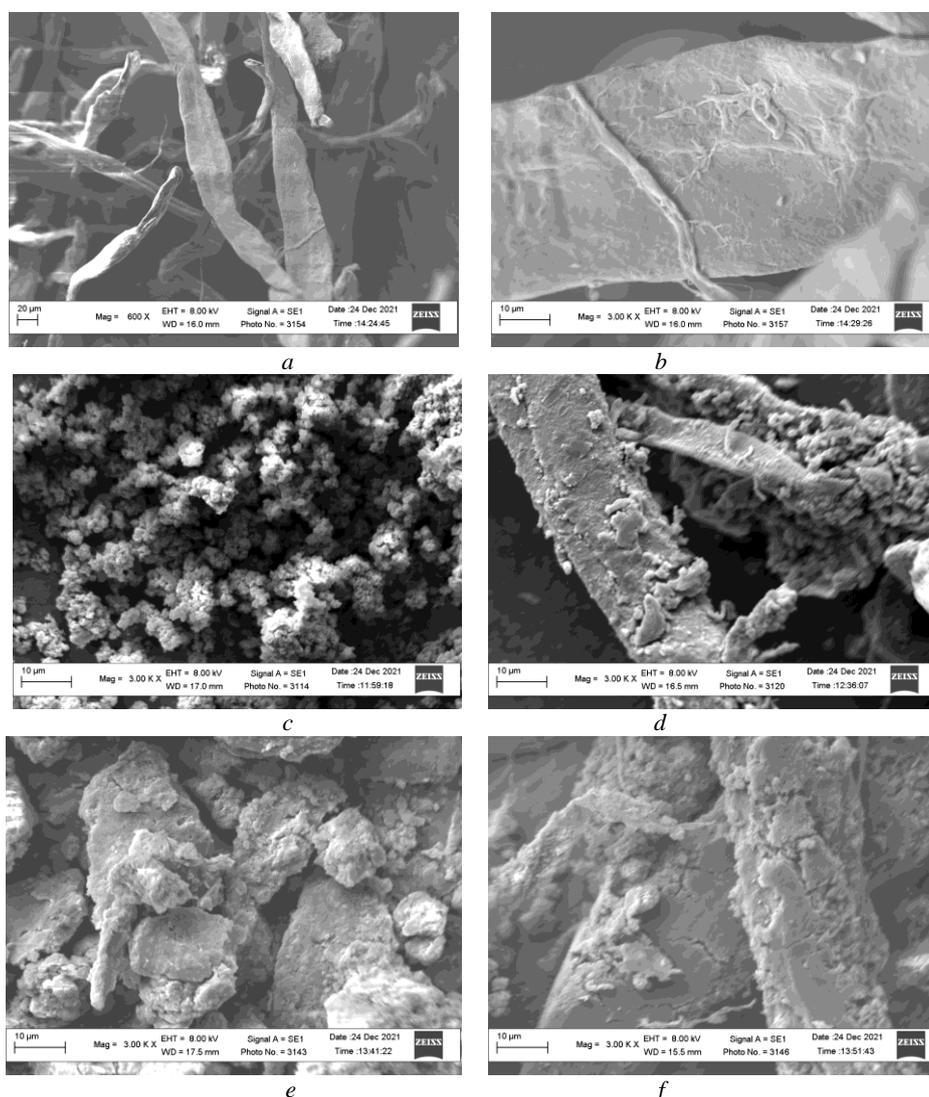

Fig. 5. SEM-images: *a*, *b* – Cel; *c*, *d* – PAn; *e*, *f* – Cel/PAn after adsorption of Cr(VI); *c, d* and e, *f* – samples were synthesized in solutions of FA and CA, respectively

Microfibrils of cellulose in all investigated composites are coated with a layer of PAn (see Fig. 5, *d*, *f*), which supplies a higher surface area of the adsorbent. In addition, H-bonded functional groups of cellulose (–OH) and amino (–NH) [26, 43, 47, 53, 56], can hold the films (layers) of PAn on the surface of cellulose microfibrils.

The presence of chromium is acknowledged by SEM images of the surface of Cel microfibrils coated with PAn (see Fig. 6) in aqueous solutions of formic and citric acids.
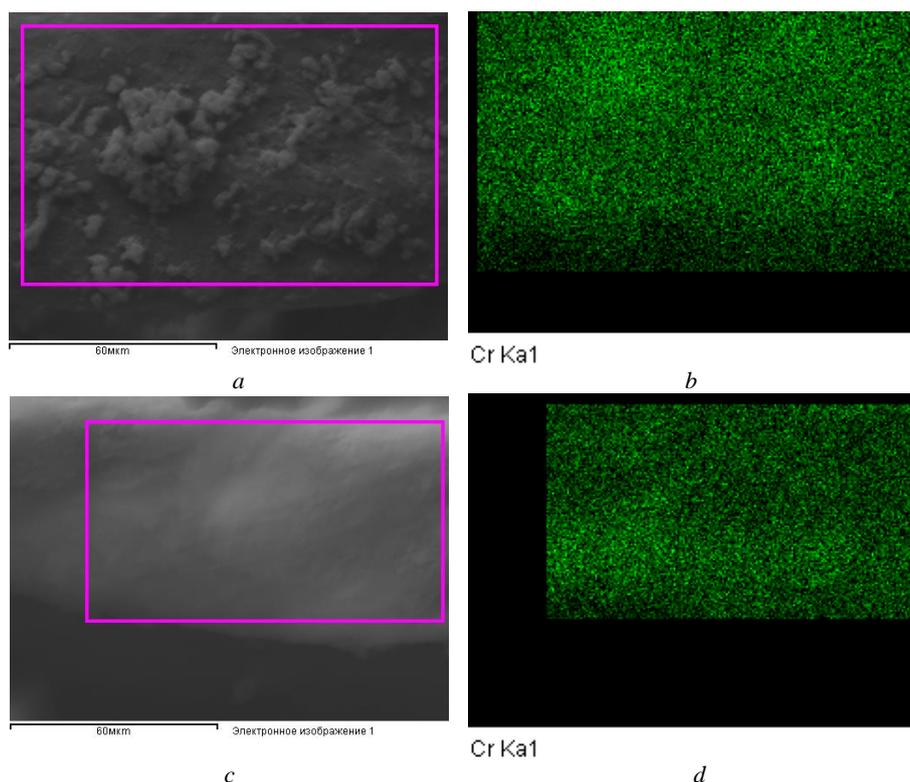

Fig. 6. SEM images of some areas of microfibrils of cellulose, coated with PAn (*a*, *c*),
and element mapping of chromium in Cel/PAn-FA and Cel/PAn-CA composite (*b*, *d*).
Employed solutions: *a*, *b* – formic acid; *c*, *d* – citric acid

As can be seen from Fig. 6, *b*, *d*, on the surface of the researched samples is a large amount of chromium. It is obviously trivalent chromium, caused to washing these samples after adsorption. Under similar conditions adsorption of Cr(VI) by a film of PAn, deposited on a polyethylene terephthalate substrate [59] and oxidation of EmS of PAn to pernigraniline has been studied.

During this investigations, pH of solutions was ~5.0–6.0, and Cr(VI) is mainly in the form of $Cr_2O_4^{2-}$, CrO_4^{2-} ions and to a lesser extent $HCrO_4^-$ [60]. Hexavalent chromium is excellently adsorbed by PAn and various composites, such as PAn/Zeolite [61] with these ranges of pH.

4. Conclusion

Some properties of the synthesized samples of polyaniline and samples of cellulose composites with poly aniline, in which polyaniline was added during the synthesis of formate, acetic, oxalic and citric acids (PAn-FA, PAn-AA, PAn-OA and PAn-CA) and (Cel/PAn-FA, Cel/PAn-AA, Cel/PAn-OA and Cel/PAn-CA), respectively.

It is shown that electrically conductive films of PAn are formed on the surface of Cel, which confirms the presence of dopant acid in the composition of PAn.

The obtained samples of polyaniline and composites were used to study their adsorption capacity in relation to chromium (VI). It was found that the removal of Cr(VI) samples PAn-FA, PAn-AA, PAn-OA and PAn-CA and samples Cel/PAn-FA, Cel/PAn-AA, Cel/PAn-OA and Cel/PAn-CA occurs practically 98–100 %.

The adsorption kinetics are satisfactorily described by equations of pseudo first and pseudo second kinetic orders. According to the research results, the Langmuir and Freundlich isotherms are constructed. It was found that the process of adsorption of chromium (VI) by PAn and Cel/PAn samples, in which PAn is supplemented with various organic acids, is best consistent with the Langmuir adsorption model. It is shown that the adsorbed chromium remains in the samples of adsorbents in the form of chromium (III).

The remarkable adsorption properties are shown by PAn-FA, Cel/PAn-FA, PAn-CA and Cel/PAn-CA. Therefore, these properties of such samples can be used for efficient absorption of Cr(VI) in drinking water.

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ПОРІВНЯЛЬНИЙ АНАЛІЗ АДСОРБЦІЙНОЇ ЗДАТНОСТІ СТОСОВНО Cr(VI) ПОЛІАНІЛІНУ ТА КОМПОЗИТІВ ЦЕЛЮЛОЗА/ПОЛІАНІЛІН, СИНТЕЗОВАНИХ У ВОДНИХ РОЗЧИНАХ ОРГАНІЧНИХ КИСЛОТ

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Окисненням аніліну (Ан) амонійпероксодисульфатом (АПС) у водних 0,5 М розчинах форміатної, ацетатної, оксалатної та цитратної кислот синтезовано зразки поліаніліну, допованого в процесі синтезу цими кислотами (ПАн-ФК, ПАн-АК, ПАн-ОК та ПАн-ЦК). За тією ж методикою тільки за наявності суспензії мікрофібрилярної вибіленої целюлози (Цел) синтезовано зразки композитів целюлози з поліаніліном, допованим у процесі синтезу тими самими кислотами (Цел/ПАн-ФК, Цел/ПАн-АК, Цел/ПАн-ОК та Цел/ПАн-ЦК). Співвідношення Ан : Цел становило 1 : 1 (г : г). Структуру отриманих зразків досліджено за допомогою Х-дифракційного, ІЧ–ФП спектрального аналізів, сканувальної електронної мікроскопії та електропровідності.

Отримані зразки поліаніліну та композитів використано для дослідження їхньої адсорбційної стосовно хром(VI) здатності. Для вивчення адсорбції використано електронну спектроскопію (УФ-В спектри) та флуоресцентний рентгенівський аналіз. З'ясовано, що видалення Cr(VI) зразками ПАн-ФК, ПАн-АК, ПАн-ОК та ПАн-ЦК та зразками Цел/ПАн-ФК, Цел/ПАн-АК, Цел/ПАн-ОК та Цел/ПАн-ЦК відбувається практично на 98–100 %.

Кінетику адсорбції задовільно описано рівняннями псевдо-першого та псевдо-другого кінетичного порядків. За результатами досліджень побудовано ізотерми Ленгмюра та Фройндліха. Визначено, що процес адсорбції хром(VI) зразками ПАн та Цел/ПАн, у яких ПАн допований різними органічними кислотами, найкраще узгоджується з адсорбційною моделлю Ленгмюра. Показано, що адсорбований хром залишається в зразках адсорбентів у вигляді хром(III).

Підтвердження адсорбції хрому досліджуваними зразками зроблено за допомогою електронної спектроскопії, флуоресцентного рентгенівського аналізу та енергодисперсійного аналізу.

Ключові слова: поліанілін, целюлоза, композити, структура, хром(VI), адсорбція.