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## ADSORPTION OF ANIONIC DYES ON CORN STALKS MODIFIED BY POLYANILINE: KINETICS AND THERMODYNAMIC STUDIES

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*Extensive use of synthetic dyes in different industries has created a major pollution problem. Among various treatments, adsorption has been considered as an effective method due to its simplicity, availability and effectiveness in removing of dyes from wastewaters. In the current work, the composite "corn stalks-polyaniline" (CS-PAN) is proposed to be used as alternative adsorbent to expensive activated carbons. We have synthesized the new composite by the chemical polymerization of aniline on the surface of corn stalks using  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  as an oxidation agent and  $\text{H}_3\text{PO}_4$  as a dopant. The composite was characterized by using Fourier infrared spectroscopy, specific surface area analysis, pH of point zero charge, bulk density, and total pore volume. In comparison with corn stalks, the composite CS-PAN had a high adsorption capacity and efficiency toward anionic dyes (Acid Red and Acid Orange) in the aqueous medium. The adsorption process attains equilibrium within 120–150 min. The adsorption of the acid dyes increased on CS-PAN composite with increase in temperature. It indicates that the adsorption is an endothermic process. Kinetic studies revealed the adsorption process was best described by the reaction model of pseudo-second order than pseudo-first order. The activation energy of adsorption was calculated as 13.1 and 7.8 kJ/mol for Acid Red and Acid Orange, respectively. Equilibrium adsorption studies of the anionic dyes on CS-PAN indicated the Langmuir equation fit better than the Freundlich equation. Maximum adsorption capacity CS-PAN was calculated at different temperatures (303, 313, and 328 K) as  $7.0 \cdot 10^{-5}$ ,  $8.3 \cdot 10^{-5}$ ,  $10.7 \cdot 10^{-5}$  and  $9.8 \cdot 10^{-5}$ ,  $12.2 \cdot 10^{-5}$ ,  $16.0 \cdot 10^{-5}$  mol/g toward Acid Red and Acid Orange, respectively. The values of the standard free energy change have been calculated as -29.6, -30.7, -32.6 for Acid Red and -30.1, -31.1, -32.7 kJ/mol for Acid Orange at 303, 313, and 323 K, respectively, which indicating that a spontaneous process occurred. Calculations indicated that the enthalpy changes of adsorption were 6.7 and 1.3 kJ/mol for Acid Red and Acid Orange, respectively. Besides, the calculated standard entropy changes of adsorption were 107 and 85 J/mol K for Acid Red and Acid Orange, respectively. Consequently, the composite CS-PAN, an inexpensive, easily synthesized, and efficient adsorbent, could be an alternative for more costly adsorbents used for removal of anionic dyes in wastewater treatment.*

**Keywords:** *adsorption, kinetics, thermodynamics, anionic dye, corn stalk, polyaniline*

### INTRODUCTION

Most industries (textile, paper, tannery, fur, pharmaceutical, cosmetic, and food) apply coloring of their products by synthetic organic dyes [1] due to their ease of use, stability and variety of color compared with natural dyes. The textile industry is in the forefront of dyes use. In this case, it is produced substantial volumes of colored wastewaters containing pollutants which may have toxic, mutagenic and carcinogenic properties [2]. Therefore, wastewaters of textile

industry have to be treated before being discharged to the environment.

Nowadays many different methods (physical, chemical, physical-chemical and biological) are used to remove dyes from wastewaters [3]. These methods often use of the expensive equipment and have plenty of disadvantages including incomplete dye removal. Among different methods adsorption is remained the most economical and widely used for removal of dyes from wastewater. Currently, there has been growing interest in finding

inexpensive and effective adsorbents alternative to expensive activated carbon. Polyaniline (PAN) shows good potential for adsorbing organic anions of acid and direct dyes from the effluents [4, 5]. This is due to the fact that PAN contains imine and amine groups which can adsorb anions via electrostatic interactions or through hydrogen bonding. However bare polyaniline particles are generally aggregated in solution. The aggregation of the particles lowers adsorption capacity of PAN and significantly influences on adsorption kinetics [6].

Adsorption capacity of bare polyaniline particles could be enhanced by polymerization of aniline on plant waste. Due to the nature of the various reactive functional groups in plant wastes they are mostly useful for uptake of cations from aqueous solutions [7]. The composites "plant waste-PAN" were obtained using rice husk [8] and sawdust [9–12]. They were researched as adsorbents for removing Cr(VI) [8] and acid dyes [9–12] from aqueous solution.

It was found [13] that modification of rice husk and sawdust by PAN had caused the increase of the surface areas of the composites from 35.7 for PAN to 38.7 m<sup>2</sup>/g for modified

rice husk and 41.3 m<sup>2</sup>/g for modified sawdust. The pores of the composites were quite big, that is why large anions could penetrate into them.

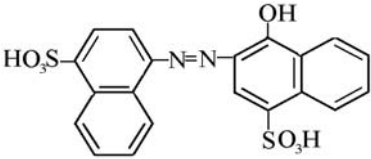
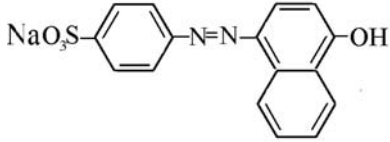
In the present paper, corn stalks were employed as a very cheap and environmentally friendly substrate for chemical modification by PAN before adsorption experiments. The aim of this study was to investigate kinetics and thermodynamics of anionic dye adsorption on corn stalks modified by PAN.

## EXPERIMENTAL

**Materials and methods.** Chemicals ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, H<sub>3</sub>PO<sub>4</sub>, HNO<sub>3</sub>, NaOH, C<sub>2</sub>H<sub>5</sub>OH) were of analytical grade and used without further purification. Aniline was of chemical grade and it was doubly distilled under vacuum. Aniline was stored below 4 °C before polymerization.

Acid Red (AR) and Acid Orange (AO) were supplied by Company Fine organic synthesis plant "Barva AG" (Ukraine). They were used without purification. The dye solutions were prepared by dissolving accurately weighted dyes in distilled water. In this investigation anionic dyes are sodium salts of sulfonic acids. Their characteristics are presented in Table 1.

**Table 1.** Characteristics of dyes

Dye	Molecular structure	Formula	Molecular mass	Van der Waals area, nm <sup>2</sup>
AR		C <sub>20</sub> H <sub>14</sub> N <sub>2</sub> S <sub>2</sub> O <sub>7</sub>	458	1.19
AO		C <sub>16</sub> H <sub>11</sub> N <sub>2</sub> O <sub>4</sub> SNa	350	0.58

The choice of the acid dyes as adsorbates was determined by the fact that among different forms of dyes (direct, acid, reactive, basic, disperse dyes) acid dyes are mainly used with the most common fibers such as wool, silk, polyamide, modified acrylic, polypropylene fibers [10]. Van der Waals areas of dye

molecules were calculated using a software package ChemAxon Marvin 5.2.

**Synthesis of PAN and CS-PAN composite.** PAN and CS-PAN composite were synthesized via chemical oxidative polymerization according to [14] with minor modification.

**Synthesis of PAN.** 200 cm<sup>3</sup> of 0.2 M (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was added dropwise with constant stirring to 200 cm<sup>3</sup> of 0.2 M aniline dissolved in 0.1 M H<sub>3</sub>PO<sub>4</sub>. After the complete addition of oxidant the reaction was kept under stirring for 5 h at 20 °C. Finally, PAN was washed with distilled water until the filtrate become colorless and dried at 50 °C.

**Synthesis of CS-PAN composite.** Corn stalks (CS) were obtained from Izmail district of Odessa region in 2014. The plant waste were dried at room temperature, milled in an electrical universal grinder and sieved to retain the fraction < 250 μm. This fraction of CS was used for preparing the modified plant waste using

polymerization of aniline. 10 g CS was added to 200 cm<sup>3</sup> of 0.2 M aniline which was dissolved in 0.1 M H<sub>3</sub>PO<sub>4</sub> and the mixture was kept for 20 h at 20 °C. Then liquid was separated from the solid phase using a Buchner funnel. 200 cm<sup>3</sup> of 0.2 M (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> was added dropwise with constant stirring to separated solid phase. After the complete addition of the oxidant, the reaction was kept under stirring for 5 h at 20 °C. Finally, the resulting composite was washed with distilled water until the filtrate become colorless and dried at 50 °C.

The characteristics of CS and CS-PAN composite are presented in Table 2.

**Table 2.** Characteristics corn stalks before and after the modification

Adsorbent	$S, \text{ m}^2/\text{g}$	$\text{pH}_{\text{PZC}}$	$\Delta, \text{ g}/\text{cm}^3$	$V_{\Sigma}, \text{ cm}^3/\text{g}$
CS	15.1	6.7	0.09	0.11
CS-PAN	46.9	3.0	0.15	0.15

In Table 2, specific surface area ( $S$ ) was calculated using the Langmuir adsorption isotherm of Acid Orange; the pH of point zero charge ( $\text{pH}_{\text{PZC}}$ ), bulk density ( $\Delta$ ) were determined as described in [14, 15]. The total pore volume ( $V_{\Sigma}$ ) of the adsorbents was determined by desiccator method using water [16].

**FTIR spectra.** CS, PAN and CS-PAN were characterized by recording their FTIR spectra (Perkin-Elmer Spectrometer). In each case, 1.0 mg of dried sample and 100 mg of KBr are homogenized using mortar and pestle thereafter pressed into a tablet.

**Adsorption studies.** Adsorption studies were carried in static conditions. In kinetic adsorption studies 0.06 g of the adsorbent (CS or CS-PAN) in 10 cm<sup>3</sup> of dye solutions (200 mg/L) at pH = 3 was shaking at 150 rpm for different time intervals. In equilibrium adsorption studies 0.06 g of the adsorbent (CS or CS-PAN) in 10 cm<sup>3</sup> of dye solutions (50–1000 mg/L) at pH = 3 was shaking at 150 rpm for 3 h. The concentrations of dyes were determined spectrophotometrically at maximum wavelengths 490 nm.

The degree of dye adsorption removal was calculated by Eq. (1)

$$\alpha = \frac{C_o - C}{C_o} \cdot 100\% , \quad (1)$$

the adsorption of dyes was calculated by Eq. (2)

$$A = \frac{C_o - C}{m} \cdot V , \quad (2)$$

where  $C_o$  is the initial dye concentration;  $C$  is the dye concentration after adsorption;  $m$  is the mass of adsorbent;  $V$  is the volume of the dye solution.

**Desorption studies.** 0.6 g of CS-PAN was added to 100 cm<sup>3</sup> of the dye solution (200 mg/L) for 3 h at pH 3 and 303 K. Afterwards, the adsorbent was thoroughly washed with distilled water and dried at 50 °C. Desorption of the dye from CS-PAN was carried out by treating 0.1 g of the composite with 100 cm<sup>3</sup> different eluents (C<sub>2</sub>H<sub>5</sub>OH (95 %), H<sub>3</sub>PO<sub>4</sub> (0.1 M), NaOH (0.1 M) and Na<sub>3</sub>PO<sub>4</sub> (1 M)) with shaking at 150 rpm for 3 h and 303 K.

The degree of dye desorption removal was calculated by Eq. (3)

$$S = \frac{C_{des} \cdot V}{A \cdot m} \cdot 100\% , \quad (3)$$

where  $C_{des}$  is the dye concentration in solution after desorption;  $V$  is the volume of eluent.

#### ADSORPTION THEORY AND MATHEMATICAL MODELS

**Kinetic models.** The experimental kinetic curves of dye adsorption on CS and CS-PAN were analyzed with the pseudo-first and pseudo-second order kinetic equations [17, 18].

The linear form of pseudo-first and pseudo-second order model equation can be expressed, respectively, by Eqs. (4) and (5)

$$\ln(A_e - A) = \ln A_e - k_1 t , \quad (4)$$

$$\frac{t}{A} = \frac{1}{k_2 A_e^2} + \frac{1}{A_e} \cdot t , \quad (5)$$

where  $A_e$  and  $A$  are the amounts of the dye on the adsorbent at equilibrium and various time  $t$ , respectively;  $k_1$  is the adsorption rate constant of pseudo-first order model;  $k_2$  is the adsorption rate constant of pseudo-second order model.

The pseudo-first order kinetic model assumes that the rate of adsorption with time is directly proportional to the difference between saturation concentration and the amount of solid uptake [9]. The pseudo-second order kinetic model assumes that the adsorption capacity of the adsorbent is proportional to the number of active sites occupied on the adsorbent surface [18].

**Adsorption models.** The Langmuir and Freundlich models are widely used for evaluating the adsorption isotherms of dyes [5, 9, 11, 12]. The linear form of isotherms is represented by Eqs. (6) and (7).

Langmuir isotherm

$$\frac{C_e}{A} = \frac{1}{A_\infty K_L} + \frac{C_e}{A_\infty} , \quad (6)$$

Freundlich isotherm

$$\ln A = \ln K_F + \frac{1}{n} \ln C_e , \quad (7)$$

where  $A$  is the amount of dye adsorbed per unit mass of the adsorbent;  $C_e$  is the equilibrium concentration of dye in solution;  $K_F$  is the measure of adsorption capacity;  $1/n$  is the

adsorption intensity;  $A_\infty$  is the amount of adsorbate at complete monolayer coverage and gives the maximum adsorption capacity of the adsorbent, and  $K_L$  is the Langmuir constant that relates to the energy of adsorption.

The Langmuir model assumes monolayer surface coverage on equivalent sites of the adsorbent. The Freundlich model assumes a heterogeneous surface of the adsorbent with sites that have different energies.

In the Freundlich model a small value of  $1/n < 1$  indicates that the adsorption is favorable over the entire range of concentration investigated. The high value of  $K_F$  also indicates the high adsorption capacity of the adsorbent. The Langmuir model assumes that the surface of the adsorbent consists of a given number of equivalent sites where the adsorbate can stick on the surface of the adsorbent through Van der Waals interactions (called physisorption) or through the formation of covalent bonds (called chemisorption) [12].

**Thermodynamics of adsorption.** Thermodynamic parameters associated with the adsorption, viz. standard free energy change ( $\Delta G^\circ$ ), standard enthalpy change ( $\Delta H^\circ$ ), and standard entropy change ( $\Delta S^\circ$ ) were calculated by Eqs. (8–10)

$$\Delta G^\circ = -RT \ln K , \quad (8)$$

$$K = K_L \cdot \gamma \cdot \frac{s_o}{s} , \quad (9)$$

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \cdot \frac{1}{T} , \quad (10)$$

where  $K$  is the adsorption constant;  $\gamma$  is the amount solvent in 1 kg of its weight (for water  $\gamma = 55.5$  mol/kg);  $s_o$  and  $s$  are areas of solvent and dye molecules occupied on the surface of the composite (for water,  $s_o = 0.0959$  nm<sup>2</sup>; for dyes, Van der Waals areas of dye molecules were listed in Table 1);  $R$  is the universal gas constant;  $T$  is the absolute temperature.

#### RESULTS AND DISCUSSION

**FTIR analysis.** Numerous studies have established that FTIR analysis is a useful tool to understand the possible interaction between the adsorbent and adsorbate. Table 3 shows the peak positions in FTIR spectra of CS, PAN and CS-PAN. The characteristic peaks due to O-H

stretching in CS and CS-PAN were observed at 3356 and 3343  $\text{cm}^{-1}$ . The peaks due to the C-H

stretching are found at 2921, 2922, and 2923  $\text{cm}^{-1}$  in CS, PAN and CS-PAN respectively.

**Table 3.** Characteristic FTIR band absorption frequencies of CS, PAN and CS-PAN composite

Peak positions	CS	PAN	CS-PAN
	Wavenumber, $\text{cm}^{-1}$		
O-H stretching	3356	–	3343
C-H stretching	2921	2922	2923
C=O stretching of carbonyl group	1734	–	1732
	1637		
N=Q*)=N	–	1565	1604
N-B**)-N	–	1489	1454
C-N stretching	–	1297	1315
C-O stretching and OH bending of alcohol and carboxylic acids	1161	–	1158
	1047	–	1044

Q\*) – quinoid ring; B\*\*) – benzene ring

The bands are observed at 1565 and 1604  $\text{cm}^{-1}$  in PAN and CS-PAN respectively, due to the stretching of N=Q=N group, whereas the bands observed at 1489 and 1454  $\text{cm}^{-1}$  in PAN and its composite are due to the stretching of N-B-N group. Comparing to the characteristic peaks of PAN, the characteristic peak of CS-PAN are shifted to lower wavenumber for N-B-N group and to higher wavenumber for N=Q=N group, suggesting the existence of interaction between PAN and cellulose and lignin from CS. The lower wavenumber for N-B-N group of CS-PAN indicates the possibility of an interaction –OH groups present in cellulose and lignin of CS, with the nitrogen sites in PAN forming hydrogen bonds between synthesized and natural polymers. It can be assumed that the higher wavenumber for N=Q=N group in CS-PAN than in CS is due to interaction between carbonyl groups of lignin of CS and the nitrogen sites present in PAN. This hypothesis requires the further confirmation through other measurements.

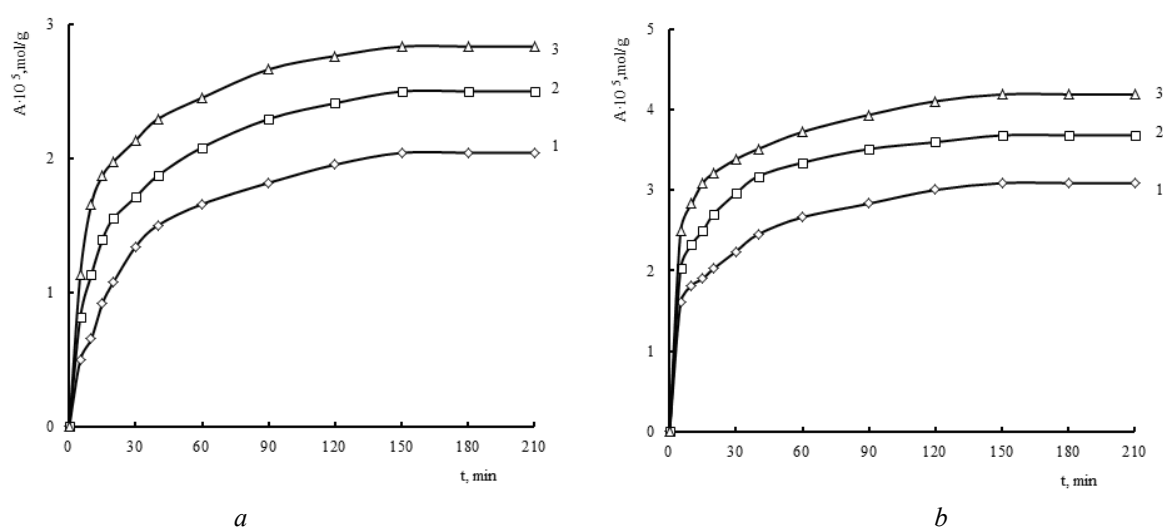
The characteristic peak for an induced delocalized  $\pi$ -electron of protonated PAN at 1297  $\text{cm}^{-1}$  is absent in CS-PAN (Table 3). This suggests that the PAN can have interact with cellulose and lignin of CS by  $\pi$ - $\pi$  overlapping of the aromatic rings. This result is in agreement with the studies reporting in [19].

**Effect of contact time.** The effect of contact time on adsorption of Acid Red and Acid Orange using CS and CS-PAN composite at different

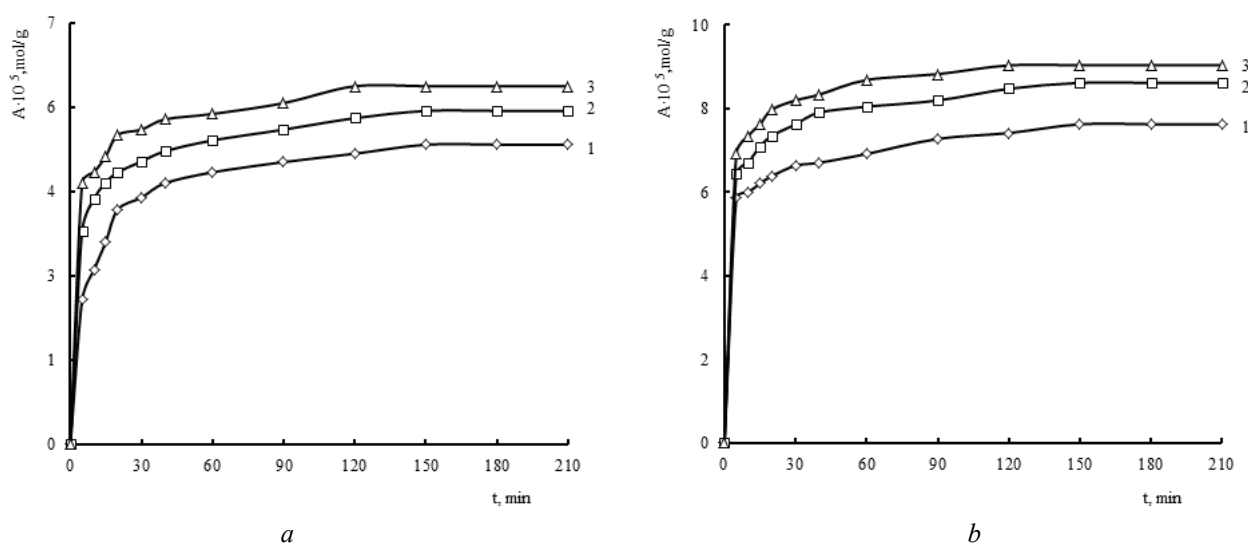
temperatures is shown in Figs. 1, 2. The equilibrium was attained within 150 min for CS at all temperatures studied and for CS-PAN at 303 K. Whereas the equilibrium was attained within 120 min for CS-PAN at 328 K. Equilibrium time as 120 min was reported for adsorption of Methyl Orange on PAN microspheres at room temperature [5].

It can be observed (Fig. 1) that there is a change of the values of dye adsorption on CS and CS-PAN if the temperature is changed. The values of dye adsorption are more increased with the increasing of temperature from 303 to 328 K on CS-PAN. It follows from the above that the adsorption the acidic dyes on CS and CS-PAN is endothermic process in nature. It can be suggested that the increase of dye adsorption on CS-PAN compared with that on CS is due to the electrostatic interactions of dyes with imine and amine groups of the composite.

It's been found out in the study [10] that the adsorption capacity of composite "sawdust-PAN" also increases with increasing the temperature. It may be due to increase in mobility of dye ions. So the number of molecules which acquire sufficient energy to undergo an interaction with active sites at the adsorbent surface is increased. Furthermore, increasing temperature may produce a swell of internal structure of composite and allow further penetrating.



**Fig. 1.** Effect of contact time on adsorption of AR (a) and AO (b) on CS at different temperatures (K): 1 – 303, 2 – 313, 3 – 328



**Fig. 2.** Effect of contact time on adsorption of AR (a) and AO (b) on CS-PAN at different temperatures (K): 1 – 303, 2 – 313, 3 – 328

**Adsorption kinetics study.** A study of adsorption kinetics is desirable as it provides information about the mechanism of adsorption, which is important for the efficiency of the process. In this study, the kinetics of the adsorption process was analyzed using the pseudo-first and pseudo-second order kinetic models. The values of rate constants and correlation coefficients for the kinetic models are shown in Table 4. The correlation coefficients calculated for the pseudo-second order kinetic model ( $R^2 = 0.999$ ) and also the good agreement of calculated values of  $A_e^{calc}$  and experimental

values of  $A_e^{exp}$  indicate that the adsorption systems follow the pseudo-second order kinetic model.

The adsorption rate constant of pseudo-second order model  $k_2$  of the dye adsorption are expressed as a function of temperature by Arrhenius equation using Eq. (11)

$$\ln k_2 = \ln A - \frac{E}{RT}, \quad (11)$$

where  $E$  is the activation energy;  $A$  is the frequency factor.

The adsorption is physisorption if the activation energy is in the range of 5–40 kJ/mol and chemisorption if it is between 40–800 kJ/mol [20]. In this study the values of activation energy of adsorption of Acid Red is 16.3 kJ/mol for CS and 13.06 kJ/mol for CS-

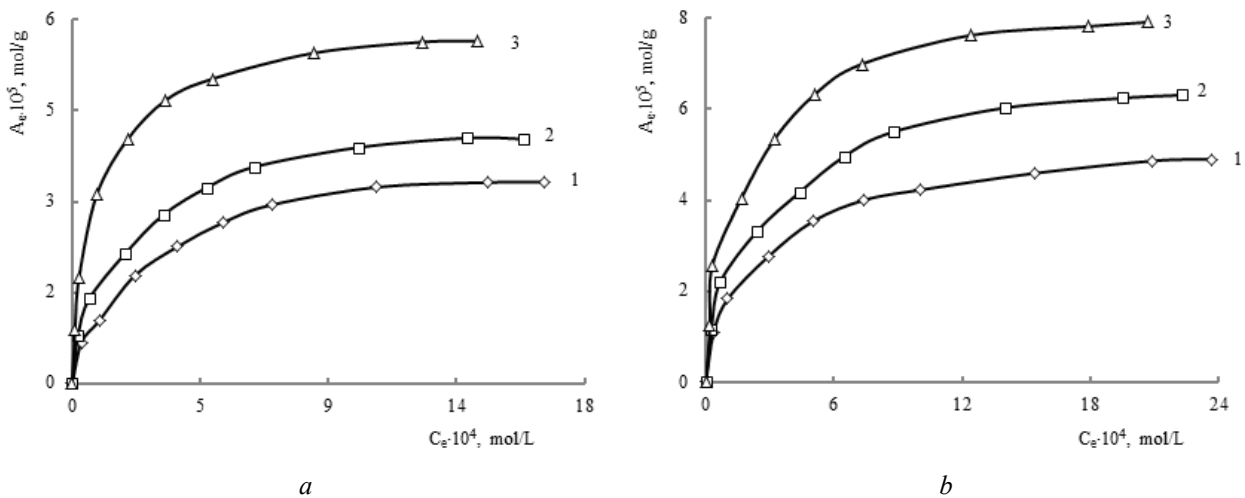
PAN. The values of activation energy of adsorption of Acid Orange is 11.0 kJ/mol for CS and 7.8 kJ/mol CS-PAN. The results obtained suggest that the adsorption of acid dyes on adsorbents is physisorption in nature.

**Table 4.** Kinetic parameters for the adsorption of acid dyes on CS-PAN

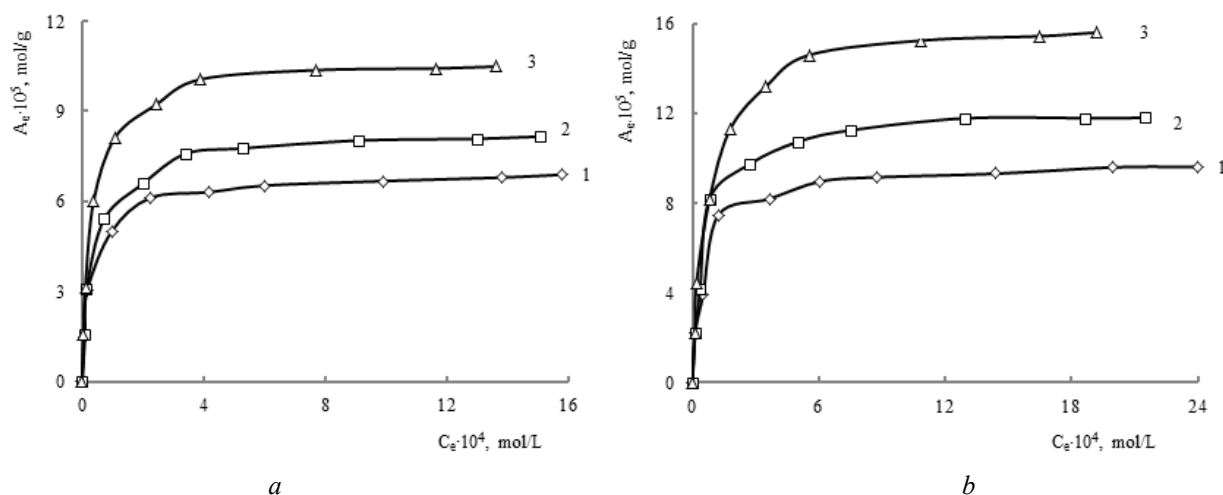
Adsorbent	Dye	T, K	$t_e$ , min	$A_e^{exp} \cdot 10^5$ , mol/g	Pseudo-first order			Pseudo-second order		
					$A_e^{calc} \cdot 10^5$ , mol/g	$k_1 \cdot 10^2$ , min <sup>-1</sup>	$R^2$	$A_e^{calc} \cdot 10^5$ , mol/g	$k_2 \cdot 10^3$ , g/(mol·min)	$R^2$
CS	AR	303	150	2.0	1.6	2.3	0.9888	2.3	2.0	0.9990
		313	150	2.5	1.6	2.4	0.9945	2.7	2.5	0.9991
		328	150	2.8	1.5	2.4	0.9765	3.0	3.3	0.9994
	AO	303	150	3.0	1.7	2.3	0.9881	3.1	2.5	0.9984
		313	150	3.6	1.7	2.6	0.9930	3.8	2.6	0.9982
		328	150	4.2	1.6	2.7	0.9836	4.3	3.5	0.9993
CS-PAN	AR	303	150	5.0	0.7	2.3	0.9491	5.2	2.3	0.9998
		313	120	5.5	0.7	2.2	0.9749	5.7	3.3	0.9996
		328	120	6.0	1.5	2.0	0.9290	6.1	4.0	0.9996
	AO	303	150	7.6	1.7	6.3	0.9937	7.8	2.9	0.9994
		313	150	8.6	1.4	7.1	0.9205	8.8	3.0	0.9997
		328	120	9.0	1.7	7.9	0.9834	9.2	3.7	0.9999

**Adsorption isotherms.** Adsorption isotherms are important for the description of how dyes interact with adsorbent surface and also are critical in optimizing the use of the new

adsorbents. The effect of different temperatures on adsorption isotherms of Acid Red and Acid Orange on CS and CS-PAN composite are shown in Figs. 3, 4.



**Fig. 3.** Adsorption isotherms of AR (a) and AO (b) on CS at different temperatures (K): 1 – 303, 2 – 313, 3 – 328



**Fig. 4.** Adsorption isotherms of AR (a) and AO (b) on CS-PAN at different temperatures (K): 1 – 303, 2 – 313, 3 – 328

It has been observed in Figs. 3, 4 that the adsorption of acid dyes on CS and CS-PAN increases if the temperature increases from 303 to 328 K. This confirms our kinetic data that the adsorption of acid dyes is an endothermic process.

These adsorption data were further analyzed with adsorption isotherm models to find out a suitable model. The Langmuir isotherm fits quite well with the experimental data with good correlation coefficient as shown in Table 5. The Langmuir adsorption capacities are increased on CS ~ in 1.6 and CS-PAN ~ in 1.5 times with the increase in temperature from 303 to 328 K. This indicates that the adsorption is favored at high

operating temperature. Similar results were reported for the removal of Acid Violet 49 by composite “sawdust-PAN” [9]. Our studies suggest also that the adsorption capacity of CS-PAN is doubled as compare with that of CS.

According to the values of  $A_{\infty}$  of the acidic dyes on CS and CS-PAN, Acid Orange is adsorbed better than Acid Red. From data in Table 1 the size of the Acid Orange ion is half of that of Acid Red ion. Thus, Acid Orange ions easily penetrate into porous structure of the composite.

Table 5 shows that the correlation coefficient values of the Freundlich model are not high compared to the Langmuir isotherm model.

**Table 5.** Isotherm parameters obtained by using linear method

Adsorbent	Dye	$T, K$	Langmuir isotherm model			Freundlich isotherm model		
			$A_{\infty} \cdot 10^5, \text{mol/g}$	$K_L \cdot 10^{-4}, \text{L/mol}$	$R^2$	$1/n$	$K_F \cdot 10^4$	$R^2$
CS	AR	303	3.6	6.07	0.9866	0.43	5.92	0.9669
		313	4.3	8.48	0.9915	0.37	5.23	0.9728
		328	5.9	16.5	0.9977	0.35	6.75	0.9265
	AO	303	5.2	5.9	0.9926	0.36	4.83	0.9697
		313	6.7	6.3	0.9915	0.37	6.84	0.9664
		328	8.3	9.1	0.9951	0.36	8.34	0.9252
CS-PAN	AR	303	7.0	2.83	0.9998	0.25	4.11	0.8429
		313	8.3	2.95	0.9997	0.27	5.74	0.8916
		328	10.7	3.44	0.9999	0.30	9.43	0.8785
	AO	303	9.8	1.67	0.9997	0.27	5.78	0.8658
		313	12.2	1.70	0.9998	0.30	8.99	0.8480
		328	16.0	1.74	0.9990	0.35	17.10	0.8751



**Thermodynamics study.** Table 6 shows the thermodynamic results for the removal of acid dyes by CS and CS-PAN. The decrease in the negative values of the standard free energy change with the increase of temperature (303 to 328 K) indicates that the adsorption becomes more favorable at high temperature. The positive values of standard enthalpy change indicate that

the adsorption of acid dyes is endothermic process. Furthermore, the positive values of standard entropy change indicate that the degrees of freedom increased at the solid – liquid interface during adsorption of acid dyes on CS and CS-PAN. According to [21], hydrophobic interactions are reason of positive values of entropy change.

**Table 6.** Thermodynamical parameters for the adsorption of acid dyes on CS-PAN

Adsorbent	Dye	T, K	$-\Delta G^\circ$ , kJ/mol	$\Delta H^\circ$ , kJ/mol	$\Delta S^\circ$ , J/(K·mol)
CS	AR	303	25.7	33.6	135
		313	27.4		
		328	30.6		
	AO	303	27.4		
		313	28.5		
		328	30.9		
CS-PAN	AR	303	29.6	6.7	107
		313	30.7		
		328	32.6		
	AO	303	30.1		
		313	31.1		
		328	32.7		

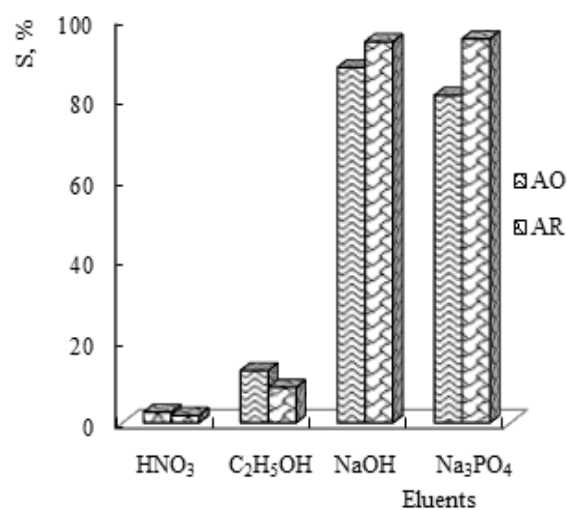
Generally,  $\Delta G^\circ$  values are between -20 to 0 kJ/mol for physisorption and they are between -80 to -400 kJ/mol for chemisorption [20]. The  $\Delta G^\circ$  values in Table 6 confirm that the adsorption of acid dyes on CS and CS-PAN is physisorption in nature.

**Desorption studies.** Desorption studies can help to elucidate the nature of adsorption process. If strong acid or base solution can desorb dyes, attachment of dyes on an adsorbent is by ion exchange and if organic solvents as alcohol cannot desorb dyes, adsorption of dyes on an adsorbent is by chemisorption [21].

It was found (Fig. 5) that the desorption percentage of Acid Red and Acid Orange was not satisfactory in case using 95 %  $C_2H_5OH$  (respectively only 8 and 13 %) and 0.1 M  $HNO_3$  (respectively only 2 and 3 %). Insignificant desorption of the dyes from surface of CS-PAN composite can be denoted to strong interactions (e.g. electrostatic attraction) between dye anions and the composite.

Maximum desorption (more than 81 %) for acid dyes was observed due to using 0.1 M  $Na_3PO_4$  and (more than 88 %) 0.1 M NaOH. The

high desorption percentage of anionic dyes from CS-PAN due to using solutions of NaOH and  $Na_3PO_4$  may imply that there is physisorption mechanism of the dye anions along with weak chemical forces of attraction on CS-PAN composite.



**Fig. 5.** Desorption of acid dyes on CS-PAN composite by different eluents

## CONCLUSIONS

CS-PAN composite was synthesized by chemical polymerization of aniline on the surface of corn stalks. The adsorption of the acid dyes increased on CS and CS-PAN composite with increase in temperature from 303 K to 328 K indicates that the adsorption is an endothermic process. The kinetic models have been calculated and the data shows that the pseudo-second order kinetic model is the best linearity with the data for more than pseudo-first order kinetic model. The values of adsorption activation energy of

acid dyes on CS and CS-PAN composite suggest that the adsorption is physisorption in nature. The data have been analyzed using isotherm models, and the data show that Langmuir model is the best linearity with the data more than Freundlich model. The negative values of standard free energy change confirmed that the adsorption of acid dyes is spontaneous. It was suggested that CS-PAN more effective than CS. CS-PAN can be used as a potential adsorbent for the removal of acid dyes from aqueous solutions.

## Адсорбція аніонних барвників на стеблах кукурудзи, модифікованих поліаніліном: кінетика та термодинамічні дослідження

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Хімічною полімеризацією аніліну на поверхні стебел кукурудзи (СК) за допомогою окиснювача  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , та допанта  $\text{H}_3\text{PO}_4$  отримано композит СК-ПАН. Його застосували як новий адсорбент для адсорбції аніонних барвників (кислотного червоного і кислотного жовто-гарячого). Вивчено кінетику та термодинаміку адсорбції барвників з водних розчинів на СК та СК-ПАН. Кінетика адсорбції барвників за допомогою СК та СК-ПАН добре описується моделлю псевдо-другого порядку. Рівноважні дані проаналізовані за допомогою рівнянь ізотерм Фрейндліха і Ленгмюра. Модель Ленгмюра краще описує експериментальні ізотерми адсорбції, ніж модель Фрейндліха. Термодинамічні розрахунки показали, що адсорбція є спонтанним і ендотермічним процесом.

**Ключові слова:** адсорбція, кінетика, термодинаміка, аніонний барвник, стебла кукурудзи, поліанілін

## Адсорбция анионных красителей на стеблях кукурузы, модифицированных полианилином: кинетика и термодинамические исследования

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Химической полимеризацией анилина на поверхности стеблей кукурузы (СК) с помощью окислителя  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  и допанта  $\text{H}_3\text{PO}_4$  получен композит СК-ПАН. Его использовали в качестве нового адсорбента для адсорбции анионных красителей (кислотного красного и кислотного оранжевого). Изучена кинетика и термодинамика адсорбции красителей из водных растворов на СК и СК-ПАН. Кинетика адсорбции красителей с помощью СК и СК-ПАН хорошо описывается моделью псевдо-второго порядка. Равновесные данные проанализированы с помощью уравнений изотерм Фрейндлиха и Ленгмюра. Модель Ленгмюра лучше описывает экспериментальные изотермы адсорбции, чем модель Фрейндлиха. Термодинамические расчеты показали, что адсорбция является спонтанным и эндотермическим процессом.

**Ключевые слова:** адсорбция, кинетика, термодинамика, анионный краситель, стебли кукурузы, полианилин

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