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Adsorption of arsenazo III dye by phosphorus-containing polymer sorbent

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Abstract: Phosphorus-containing polymer sorbent was used for removal of hazardous arsenazo III dye from water. The adsorption characteristics were determined by studying the effect of different parameters such as solution pH, initial dye concentration, sorbent dose, phase contact time and temperature. The equilibrium data were analyzed by using Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) adsorption isotherm models. The highest monolayer adsorption capacity (24.75 mg g^{-1}) has been obtained at 55 °C. Different thermodynamic parameters such as free energy, enthalpy and entropy changes have been calculated. It was concluded that when the temperature rises, the adsorption increases, indicating the endothermic nature of the process. Kinetic parameters were derived by using pseudo-first-order, pseudo-second-order and intraparticle kinetic models. Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) were used to characterize the sorbent and to validate the adsorption mechanism.

Keywords: dye; removal; polymeric sorbent; equilibrium; kinetics; thermodynamics.

INTRODUCTION

Dyes, generally are synthetic organic compounds, which have complex molecular structure and high molecular weight. These properties increase the difficulties of wastewaters treatment. It is well known that the wastewaters containing dyes are poisonous, carcinogenic and teratogenic to humans. Therefore, the efficient disposal of dyestuff in wastewaters has attracted wide attention.[1] The methods employed for removal of dyes from contaminated wastewaters include coagulation/flocculation,[2] biological oxidation,[3] membrane processes,[3] solvent extraction,[4] adsorption[5] and ion exchange.[6] Most of these techniques have significant disadvantages including incomplete dye removal, high reagent and energy necessity, low selectivity, high capital and operational cost and generation

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of secondary wastes that are difficult to dispose. On the other hand, the usage of one individual technique is not sufficient to achieve complete decolorization. Therefore, dye removal strategies consist of a combination of different techniques. In comparison to other techniques, the adsorption is superior in simplicity of design, initial cost, ease of operation and insensitivity to toxic substances. This technique uses a large number of suitable sorbents such as activated carbon,[7] low cost adsorbents (natural, industrial, as well as synthetic materials/ /wastes)[8] and polymeric materials (sorbent and resins).[9]

The azo dyes constitute the largest chemical class, containing at least 66 % of all colorants. Their characteristic feature is the presence in their structure of one or more azo groups, together with hydroxyl groups, amine and substituted amine groups serving as auxochromes. They have found a broad range of application in the pharmaceutical, cosmetic, food, dyeing/textile industry and analytical chemistry.[10] One representative of the azo dyes is arsenazo (III) (AR, bis-azo derivative of chromotropic acid containing arsenic), which is widely used for spectrophotometric determination of metal ions and proteins.[11-18] AR is a hazardous chemical compound, which may cause cancer when inhaled, ingested or exposed to *via* the eye or skin. The threshold value for AR is 0.5 mg L^{-1} in aqueous medium.[19] This makes the investigation of the process of removing the AR from aqueous medium an urgent problem, especially since the information regarding this in the literature is scarce.[20]

The goal of this work was to study the efficiency of phosphorus-containing polymer sorbent (PhCS) used for removal of AR from aqueous solutions. The synthesis of PhCS by chemical modification (oxidative chlorophosphorylation reaction) of industrial polymer – butadiene rubber (BR) was developed by our group and was described previously.[21] It was established that this reaction can be performed using readily available commercial reagents under mild conditions and by using simple equipment. In this work the effect of different parameters such as the initial dye solution's concentration, solution pH, sorbent dose, phase contact time, and temperature was studied. Equilibrium, kinetic and thermodynamics analysis were conducted for better understanding of the adsorption process. To obtain more information about the adsorption mechanism, scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) were used.

EXPERIMENTAL

Reagents

The PhCS was used as an adsorbent for studying the adsorption behavior of AR in aqueous solution. The PhCS was synthesized on the base of BR by using PCl_3, CCl_4, H_2SO_4, acetone and O_2.[21] BR was purchased from Voronezh Synthetic Rubber Manufactory (Russia). PCl_3, CCl_4, H_2SO_4 and acetone (p.a.) were purchased from Vecton (Russia) and were used without further purification.

AR ($(HO)_2C_{10}H_2(SO_3H)_2(N{=}NC_6H_4AsO_3H_2)_2$), Fig. 1, has molecular weight of 776.4 g mol^{-1} and absorbance maximum (λ_{max}) of 530 nm. The ionizable groups have the following pK_a values:[22] pK_1 = –2.5; pK_2 = 0, pK_3,pK_4 = 2.5; pK_5,pK_6 = 5.3; pK_7 = 7.5; pK_8 = 12.4, where K_1 and K_2 refer to sulfonic acid, K_3, K_4, K_5 and K_6 refer to arsenic acid and K_7 and K_8 to hydroxyl groups respectively. The pH of the solution was maintained by using HCl and NaOH. AR, HCl and NaOH were analytical reagent grade chemicals (Gorex Analyt GmbH).

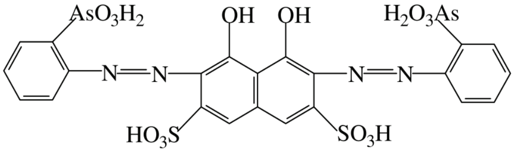

Fig. 1.The structure of AR.

Preparation of phosphorus-containing polymer sorbent[21]

A 5 % solution of BR in CCl_4 was prepared. After that PCl_3 was added to the reaction mixture at a mass ratio of 1:5 (BR:PCl_3) and the reaction system was purged with oxygen, which was supplied to the reaction medium through the concentrated H_2SO_4 at a rate of 7 L h^{-1}. The reaction was conducted for 8 h. After this, the product of the reaction (solid phase, modified BR) was separated from the liquid phase (CCl_4, $POCl_3$ and PCl_3). Then the modified BR was added to the icy distilled water, whereupon the polymer was separated and the hydrolysis process (at 50 °C for 4 h with continuous stirring) was carried out. The final product was filtered, washed with distilled water until neutral pH was reached, washed with acetone and dried firstly in air and then under vacuum at 40 °C.

Preparation and analysis of AR solutions

The stock solution of AR was prepared in deionized water (c_o = 1000 mg L^{-1}). The required concentrations of the AR solutions were prepared by appropriate dilution of the stock solutions. The remaining concentrations of AR were determined by using a double beam UV–Vis spectrophotometer (Specord 210 Plus, Analytik Jena AG, Germany) at wavelength of 530 nm.

Adsorption studies

The influence of the solution pH, sorbent dose, contact time, temperature, and initial concentration on the adsorption of AR on the PhCS, was investigated. For this purpose, at the beginning, preliminary experiments were carried out. Accurately weighed amounts of PhCS (0.03–0.60 g) have been placed into bottles and filled up with solutions of AR with different initial concentrations. Herewith the initial concentrations of 13 AR samples have been changed in the range between 5 and 120 mg L^{-1}. Experiments for each solution were performed at values of pH from 1 to 9 and at temperatures of 25, 35, 45 and 55 °C. The total volume of the solution for each experiment was 100 mL. The bottles were agitated in a temperature-controlled shaker (IKA, Germany) for 24 h. After this time, the solutions have been filtrated and the concentration of AR in the filtrate has been determined. The adsorption capacity (q / mg g^{-1}) and adsorption degree (R / %) has been calculated by using Eqs. (1) and (2):

$$q = (c_0 - c_e)\frac{V}{m} \tag{1}$$

$$R = \frac{100(c_0 - c_e)}{c_0} \tag{2}$$

where c_0 and c_e are the initial and equilibrium concentrations of AR in the solution respectively, mg L^{-1}, V is the solution volume (L) and m is the sorbent dose (g).

The results showed that for studying the influence of pH on the adsorption of AR is sufficient to conduct experiments by using dye solution with an initial concentration of 60 mg L^{-1} at adsorbent concentration of 3.3 g L^{-1}. A dye solution with similar initial concentration was chosen for studying the effect of the sorbent dose on the adsorption process, wherein the pH of the solutions was equal to 1.

The effect of the temperature and the AR initial concentration on the adsorption process was studied at the same values of pH (pH 1). Each dye concentration was allowed to interact with the similar amount of PhCS (m = 0.33 g). The adsorption isotherms were determined based on the results. The equilibrium data of the adsorption of AR were fitted to the Langmuir,[23] Freundlich,[24] Temkin,[25] and Dubinin-Radushkevich (D–R)[26] models to understand the processes governing the dye adsorption on the PhCS. The equations of used models are given in formulas (3)–(6):

$$\text{Langmuir isotherm: } q_e = \frac{q_{max} K_L c_e}{1 + K_L c_e} \tag{3}$$

$$\text{Freundlich isotherm: } q_e = K_F c_e^{1/n} \tag{4}$$

$$\text{Temkin isotherm: } q_e = B\ln A + B\ln c_e;\ q_e = B \ln A + B \ln c_e \tag{5}$$

$$\text{D–R isotherm: } q_e = q_s e^{-\beta \varepsilon^2} \tag{6}$$

In Eq. (3), q_{max} constant is the adsorbent's maximum monolayer adsorption capacity (mg g^{-1}) and K_L is the adsorption constant (L mg^{-1}) and is related to the Gibbs energy of adsorption.

In Eq. (4), K_F and n are the Freundlich constants that indicate the relative capacity and the adsorption intensity, respectively.

In Eq. (5), A denotes the Temkin constant used to examine the adsorbate–adsorbate interactions and B is the constant related to the heat of adsorption.

In Eq. (6), q_s is the theoretical isotherm saturation capacity (mg g^{-1}), β is a constant related to the sorption energy, and ε is the Polanyi potential, which is related to the equilibrium concentration through the following equation:

$$\varepsilon = RT \ln(1 + \frac{1}{c_e}) \tag{7}$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature (K).

The constant β gives the mean free energy of sorption (E) per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution. The mean free energy of sorption can be calculated by using the following equation:

$$E = \frac{1}{\sqrt{2\beta}} \tag{8}$$

The thermodynamic parameters of adsorption were determined by using the classical thermodynamic equations.[27]

To identify the contact time effect on the adsorption process, the choice of the experiment conditions was based on the preliminary experiment (mentioned above): temperature, 25 °C, initial AR concentration, 60 mg L^{-1}, PhCS dose, 0.33 g, contact time, 120 min, pH 1. Samples were obtained from the solution at set times and the dye concentration in the samples was determined. In order to analyze the experimental data and to evaluate the kinetics of the adsorption process, pseudo-first-order, pseudo-second-order, and intraparticle diffusion models were employed.[28-30]

The obtained results were statistically processed by using standard methods.[31,32] The average experimental error was estimated to be less than 4 %.

FTIR spectroscopy

The FTIR spectra for the sorbent, dye and the dye attached to the sorbent were recorded using a Thermo Nicolet iS10 FTIR spectrometer (Thermo Scientific, USA) with ATR equipment (SMART iTX). The samples were analyzed after vacuum drying. The obtained spectra were baseline corrected and normalized using an Omnic, v. 9.0, software (Thermo Scientific).

Scanning electron microscopy

SEM was used for structural characterization of the sorbent before and after the dye attachment. The SEM studies were performed on a JEOL JSM 6610LV instrument. The samples were fixed on carbon film supports. The samples were covered with platinum. The system offers a magnification 1000× and has a resolution of 3.0 nm at 30 KV in the high vacuum mode.

RESULTS AND DISCUSSION

Description of the reaction and characterization of the phosphorus-containing polymer sorbent

The synthesis of PhCS was described elsewhere in details.[21] It is to emphasize that during the modification reaction of the polymer, cross-linking process occurred between the macromolecular chains. As a results we obtained cross-linked products with different functional groups such as: $–P(O)Cl_2$ (phosphonyldichloride) and $–OP(O)Cl_2$ (phosphoryldichloride), which by the hydrolysis reaction were transformed to a phosphonate ($–P(O)(OH)_2$) and phosphate ($–OP(O)(OH)_2$) groups, respectively. The nature and distribution of functional groups in the polymer matrix, as well as the nature of the spatial network in PhCS was studied by means of NMR spectroscopy in the solid phase.[33]

The synthesized PhCS was a dark-brown powder with a cross-linked structure and was insoluble in organic solvents, mineral acids and alkalis. Its physicochemical properties are listed in Table I.[33,34]

TABLE I. Physicochemical properties of PhCS

Characteristic	Type
Ionic form	H^+
Total exchange, equiv/kg of dry sorbent	9.3
Ionization constants: pK_{a1}, pK_{a2}	4.4, 8.6
Size of particles, mesh	30–40

Effect of the solution pH

The solution pH is one of the most important experimental factors that determine the sorption selectivity in the adsorption process on sorbents. The pH value determines the specific adsorbent surface charge, the ionic dissociation of dye in solution, and the distribution of ionized species between phases.[22,35] This physicochemical parameter is important for phosphorus-containing sorbent, including polymers due to its affect to the degree of protonation and dissociation of the functional groups.[34]

The effect of the solution pH on the adsorption of AR is shown in Fig. 2. It can be seen that increase in the solution pH from 1 to 9 led to decrease of R from 86.5 to 25.9 %. The highest values of removal efficiency were obtained in acidic solutions (pH 1–2). This is due to the fact that at low pH values (pH < 3) the functional groups of the PhCS are protonated.[34] Moreover, the molecular complex of the dye is partially ionized due to the sulfonic acid groups (pK_1 = –2.5, pK_2 = 0).[22] This causes the adsorption process that takes place due to the coordination interaction between the uncharged (unionized) arsenic acid and the hydroxyl groups of the dye with the −P=O groups of the sorbent.

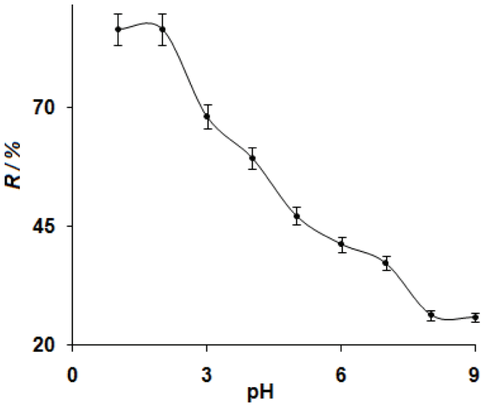

Fig. 2. Effect of the solution pH on the AR adsorption by PhCS; initial AR concentration, 60 mg L^{-1}, PhCS concentration, 3.3 g L^{-1}, contact time, 120 min, temperature, 25 °C.

The removal efficiency decreases at high pH values, due to abundance of OH$^-$ and the competition for AR anions and/or because of ionic repulsion between the negatively charged functional groups of sorbent and the anionic dye molecules.

As shown in Fig. 1, AR molecules have hydroxyl and azo groups. Due to this fact, AR exhibits tautomerism, a process in which the molecule exists in two or more different structures in equilibrium. The hydrogen atom of the hydroxyl group is able to migrate to the nitrogen atom of the azo group. This type of tautomerism involves equilibrium between a hydroxy azo tautomer and quinone hydrazone tautomer, although the quinone hydrazone tautomer generally dominates.

Due to AR structure (Fig. 1) this is possible at high pH values (>7). This provides a partial sorption in this interval of pH solution.

As a result, for further sorption experiments, an initial pH of 1.0 was selected.

Effect of the sorbent dose on sorption properties

Figure 3 shows the effect of sorbent dose on the adsorption degree. As could be seen from Fig. 3, the adsorption degree value increased with increasing of the sorbent dose until reaching an equilibrium value after 0.33 g (which corresponds to 86.0 % of the initial dye amount adsorbed onto PhCS). The increase of the adsorption degree could be assigned to the increase of the number of active functional groups, which resuled in the availability of more adsorption sites. Therefore, in the following experiments, the sorbent dose was fixed at 0.33 g.

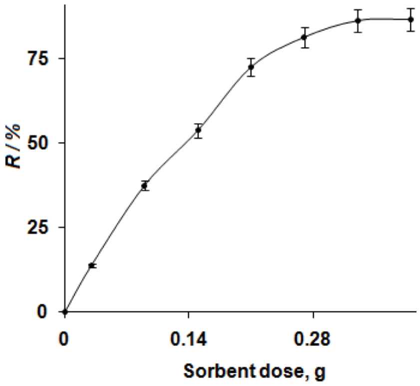

Fig. 3. Effect of PhCS dose on the AR adsorption degree; initial AR concentration, 60 mg L^{-1}, contact time, 120 min, temperature, 25 °C, pH 1.

The effect of contact time

The experiments showed that the adsorption of AR occurs rapidly at initial stages and becomes slower near the equilibrium. Figure 4 presents the plot of the adsorption degree of AR versus contact time at the selected conditions (see experimental part). As could be seen from Fig. 4, there was no considerable change of the adsorption degree of the dye after 60 min.

Effect of the initial AR concentration and temperature

During the adsorption processes, the initial concentration of adsorbates in the solution is a major factor affecting their distribution between the solid and the liquid phase. Besides this, investigation of this effect at different temperatures allowed to get additional information about the mechanism of the adsorption process.[35] Hence, the influence of the initial concentration on the adsorption was investigated while taking into consideration the temperature effect. The results of this study are shown in Table II.

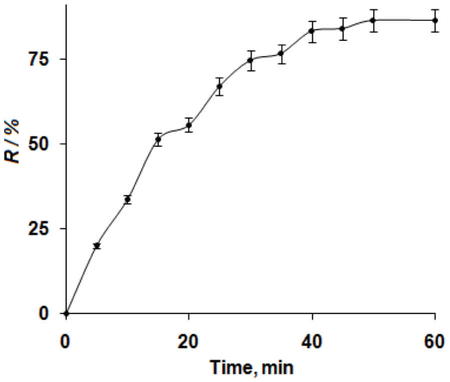

Fig. 4. Effect of contact time; c_0 = 60 mg L^{-1}, sorbent dose, 0.33 g/100 mL, pH 1.

TABLE II. The adsorption capacities and adsorption degrees at different temperatures and initial concentrations and temperatures for AR

c_0 mg L^{-1}	Temperature, °C							
	25		35		45		55	
	q_e mg g^{-1}	R %	q_e mg g^{-1}	R %	q_e mg g^{-1}	R %	q_e mg g^{-1}	R %
5	1.43±0.05	94.4±3.6	1.47±0.06	96.8±3.7	1.48±0.06	97.6±3.7	1.52±0.06	100.0±3.8
10	2.78±0.11	91.7±3.5	2.88±0.11	95.0±3.6	2.92±0.11	96.5±3.7	3.00±0.11	98.9±3.8
15	4.01±0.15	88.1±3.3	4.18±0.16	92.0±3.5	4.38±0.17	96.3±3.7	4.49±0.17	98.8±3.8
20	5.33±0.20	88.0±3.3	5.51±0.21	91.0±3.5	5.70±0.22	94.0±3.6	5.92±0.22	97.7±3.7
30	7.97±0.30	87.7±3.3	8.23±0.31	90,5±3.4	8.42±0.32	92.6±3.5	8.77±0.33	96.5±3.7
40	10.61±0.40	87.5±3.3	10.80±0.41	89.1±3.4	11.20±0.43	92.4±3.5	11.53±0.44	95.2±3.6
50	13.20±0.50	87.1±3.3	13.45±0.51	88.8±3.4	13.80±0.52	91.1±3.5	14.06±0.53	92.8±3.5
60	15.72±0.60	86.5±3.3	16.08±0.61	88.4±3.4	16.36±0.62	90.0±3.4	16.86±0.64	92.7±3.5
70	17.93±0.68	84.5±3.2	18.45±0.70	87.0±3.3	18.69±0.71	88.1±3.3	19.14±0.73	90.2±3.4
80	19.58±0.74	80.8±3.1	20.45±0.78	84.4±3.2	21.08±0.80	87.0±3.3	21.70±0.82	89.5±3.4
90	20.56±0.78	75.4±2.9	21.61±0.82	79.2±3.0	22.99±0.87	84.3±3.2	23.41±0.89	85.8±3.3
100	21.14±0.80	69.8±2.7	22.78±0.87	75.2±2.9	24.24±0.92	80.0±3.0	25.15±0.96	83.0±3.2
120	21.18±0.80	58.2±2.2	23.10±0.88	63.5±2.4	24.85±0.94	68.3±2.6	25.76±0.98	70.8±2.7

At relatively low initial concentrations of dye (c_0 < 60.0 mg L^{-1}), the adsorption degree was high (R > 85 %). In this range of concentrations, the adsorbate molecules may interact with active sites of the PhCS, and therefore the adsorption degree was relatively high. The adsorption degree decreases with increasing the initial concentration of AR. It was observed that with increase of the dye initial concentration the adsorption capacity of PhCS had larger values. As could be seen from the results, q_e is stabilized at the higher concentrations. This indicates that PhCS has a limited number of active sites for the adsorption, and at lower concentrations, almost all the dye molecules were adsorbed on the surface. However, increase in the initial AR concentration lead to rapid saturation of the sorbent surface. Besides this, with an increase of the temperature from 25 to 55 °C both the adsorption degree and the adsorption capacity increased. This result could be attributed to an increase of the AR molecules mobility and an increase the number of active sites on the sorbent surface. On the other hand, in the nature the adsorption of AR on PhCS is an endothermic process and may involve chemical sorption. Endothermic nature of the adsorption of pollutants have also been reported in other several studies, *i.e.*, in the sorption of Pb^{2+} on the cellulose-based sorbent, sphagnum moss peat, the adsorption of Pb^{2+} on the phosphate-modified kaolinite clay, the sorption of Cu^{2+} on the tree fern and the adsorption of water-soluble dye reactive brilliant blue KN-R on the functionalized resin.[36–39]

Equilibrium modelling

The equilibrium relation between adsorbent and adsorbate is defined by adsorption isotherms, which serve to describe how the adsorbed molecules interact with the adsorbents when the process approaches equilibrium. The results obtained in this study were analyzed using the Langmuir, Freundlich, Temkin and D–R isotherm equations.

All obtained isotherm constants and correlation coefficients are listed in Table III.

TABLE III. Parameters for arsenazo III adsorption by PhCS according to different equilibrium models

Isotherm model	Parameter	Temperature, °C			
		25	35	45	55
Langmuir	K_L / L g^{-1}	0.162±0.006	0.203±0.008	0.273±0.010	0.554±0.021
	q_{max} / mg g^{-1}	24.75±0.94	26.32±1.00	27.62±1.05	26.88±1.02
	r^2	0.9838±0.0374	0.9887±0.0376	0.9929±0.0377	0.9916±0.0377
Freundlich	K_F	3.471±0.132	4.406±0.167	5.470±0.208	8.377±0.318
	n	1.720±0.065	1.829±0.070	1.903±0.072	2.548±0.097
	r^2	0.9360±0.0356	0.9586±0.0364	0.9684±0.0368	0.9753±0.0371
Temkin	A	2.296±0.087	3.504±0.133	5.053±0.192	11.166±0.424
	B	4.861±0.185	4.775±0.181	4.836±0.184	4.416±0.168
	r^2	0.9166±0.035	0.9147±0.0348	0.9364±0.0356	0.9580±0.0364
D–R	q_s/ mg g^{-1}	12.57±0.48	13.20±0.50	14.55±0.55	17.24±0.66
	$\beta\times10^7$	2.0±0.08	1.0±0.04	0.8±0.03	0.5±0.02
	E / kJ mol^{-1}	1.581±0.060	2.236±0.085	2.500±0.095	3.162±0.120
	r^2	0.6225±0.0237	0.6362±0.0242	0.7204±0.0274	0.7815±0.0297

For the all four investigated systems, the Langmuir isotherm correlated with the experimental data of adsorption equilibrium of AR on PhCS better ($r^2 > 0.980$) than the Freundlich, Temkin and D–R isotherms did. The adsorption data of dye in accordance with the Langmuir isotherm show that the binding energy of the entire surface of PhCS is uniform. By the way, the whole surface has an identical adsorption activity. The adsorption data of AR in accordance with Langmuir isotherm also show that the adsorbed dye molecules do not interact or compete with each other, and they form a monolayer. This phenomenon also indicates that chemisorption has the principal removal mechanism in the adsorption process. The maximum adsorption ($q_{\max}$) values for AR are in good agreement with the experimentally obtained values.

The values of K_F and $1/n$ at temperature of 25 °C were 3.471 and 0.5814 respectively, with a correlation coefficient (r^2) of 0.9360. By increasing the temperature, the values of K_F increased and at 55 °C reached 8.377. The value of $1/n$ of 0.5814 shows that 58.14 % of the active sites on the surface of the PhCS had equal energies,[40] which decreased by increasing the temperature.

The calculated values of Temkin isotherm constants also confirm chemisorption on the sorbent surface (correlation coefficients > 0.91).

As could be seen from Table III, the D–R theoretical monolayer saturation capacity (q_s) for AR was 12.57 mg g^{-1} with a correlation coefficient (r^2) of 0.6225 at temperature of 25 °C. The value of $q_{\max}$ derived from the Langmuir model was higher than the value of the q_s derived from D–R model. The difference between $q_{\max}$ and q_s is large, which may be explained by the definitions of $q_{\max}$ and q_s in the two models. In the Langmuir model, $q_{\max}$ represents the maximum adsorption of AR at the monolayer surface, whereas in the D–R model represents the maximum adsorption of AR at the sorbent's total specific micropore volume. Thus, the value of $q_{\max}$ is higher than the value of q_s.[41] Differences between these values for other temperatures have been found.

Table III also shows that the value of E is between 1 and 4 kJ mol^{-1} and that the sorption process is a physical adsorption process. The regression parameter r^2 (0.6–0.8) showed that this isotherm model did not provide a very good fit to the experimental data.

On the basis of the received data the Langmuir isotherm essential characteristics were applied for calculation of the separation factor constant (R_L), which indicates the possibility of the adsorption process to proceed:[42] $R_L < 1$, unsuitable; $R_L = 1$, linear; $0 < R_L < 1$, suitable; $R_L = 0$, irreversible. The value of R_L was calculated by using the relation:

$$R_L = \frac{1}{1 + K_L c_0} \tag{9}$$

The values of R_L at 25, 35, 45 and 55 °C are between 0.010 and 0.554, indicating the suitability of PhCS for the removal of AR.

A comparison of the $q_{\max}$ of AR with various adsorbents reported in literature is shown in Table IV.

Although the PhCS adsorption capacity for AR is lower than the adsorption capacity of MWCNT shown in Table IV, it is higher than the one of AC. According to the obtained results, PhCS could be employed as an adsorbent for AR.

TABLE IV. Comparison of $q_{\max}$ of PhCS with adsorbents reported for AR

Adsorbent	$q_{\max}$ / mg g^{-1}	Reference
Phosphorus-containing polymer sorbent	24.75	Present work
Activated carbon (AC)	10.20	20
Multiwalled carbon nanotubes (MWCNT)	30.58	20

Determination of thermodynamic parameters

The equilibrium constants obtained from the Langmuir model at 25, 35, 45 and 55 °C were used to determine the thermodynamic parameters.

The values of K_L at different temperatures were processed by using van't Hoff equation. $\Delta H^\ominus$ and $\Delta S^\ominus$ can be determined from the slope and intercept of the plot of lnK versus T^{-1} (Fig. 5).

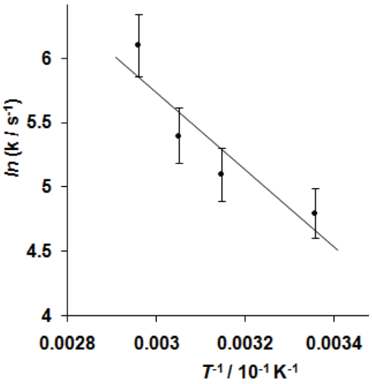

Fig. 5. ln *K vs.* 1/*T* plot.

The values of $\Delta H^\ominus$ and $\Delta S^\ominus$ are listed in Table V. The positive values of $\Delta H^\ominus$ show endothermic nature of adsorption, while positive values of $\Delta S^\ominus$ indicate the increasing randomness at the polymer-solution interface during the process.[27]

TABLE V.Thermodynamic parameters for the adsorption of arsenazo III by PhCS.

T / °C	$-\Delta G^\ominus$ / kJ mol^{-1}	$\Delta H^\ominus$/ kJ mol^{-1}	$\Delta S^\ominus$ / J mol^{-1} K^{-1}	$T\Delta S^\ominus$ / kJ mol^{-1}	r^2
25	11.62±0.44	23.26±0.88	117.06±4.44	34.88±1.33	0.8370±0.0318
35	12.79±0.49			36.05±1.37	
45	13.96±0.53			37.23±1.41	
55	15.33±0.58			38.40±1.46	

The $\Delta G^\ominus$ values were calculated at different temperatures (Eq. (10)) and are also reported in Table V. The negative values of $\Delta G^\ominus$ indicate that the adsorption reaction occurs spontaneously. The data given in Table V also show a slight change in the values of $T\Delta S^\ominus$ at all temperatures and $|\Delta H^\ominus| < |T\Delta S^\ominus|$. This indicates that the entropy rather than the enthalpy changes dominate the adsorption process.

Kinetic modelling

Using the appropriate equations and plots, the parameters of three different kinetic models (pseudo-first-order, pseudo-second-order and intraparticle diffusion models) were calculated, and are summarized in Table VI. A good correlation of the kinetic data explains the adsorption mechanism of the AR on the solid phase.

TABLE VI. Kinetic parameters for AR adsorption by PhCS

Pseudo-rirst-order model			Pseudo-second-order model			Intraparticle diffusion model		
k_1 min^{-1}	Q_1 mg·g^{-1}	r^2	k_2×10^3 g mg^{-1} min^{-1}	q_1 mg g^{-1}	r^2	k_i mg g^{-1} min$^{-1/2}$	C	r^2
0.084	23.808	0.9562	1.663	23.810	0.9773	1.418	5.809	0.9353
±0.003	±0.905	±0.0363	±0.063	±0.905	±0.0371	±0.054	±0.221	±0.0356

Based on the correlation coefficients, the equation of the pseudo-second-order model seems to be the most suitable for the experimental kinetic data, suggesting the chemical sorption to be the rate-limiting step of the mechanism of adsorption without involvement of a mass transfer in solution.[28–30]

FTIR spectroscopy and SEM studies

In accordance with other literature information, structural characterization of the polymers (sorbents, resins) before and after dyes adsorption was performed by using FTIR spectroscopy and SEM analysis.[43,44] The FTIR measurements show presence of the following groups for PhCS (Fig. 6, spectrum 1): O−H (3343 cm^{-1}; stretch vibration), C−H aliphatic (2978 and 2935 cm^{-1} stretch vibration), O−H in P−O−H (2862 and 2494 cm^{-1} stretch vibration), P=O (1622 cm^{-1} resonance state), P=O (1183 cm^{-1} stretch vibration), C−O−P (1050 cm^{-1} stretch vibration), P–OH (1040–910 cm^{-1}) respectively. In the spectrum of AR (Fig. 6, spectrum 2) 1600–1400 cm^{-1} and 900–650 cm^{-1} region IR bands can be assigned to aromatic rings. The IR bands in the region of 1050–1350 cm^{-1} can be attributed to sulfo groups. The IR band at ~1030 cm^{-1} is attributed to the OH vibration. After AR adsorption (Fig. 6, spectrum 3), the changes occurred mainly in the P=O and P–OH groups. The signals for those groups were changed and their maximum becomes more pronounced. In general, the biggest changes were observed in the region between of 900–1750 cm^{-1}. This indicates that the process of sorption involved mainly P=O and P–OH groups. All of these alterations are a clear indication of interactions that took place between AR and the PhCS.

SEM micrographs of PhCS and AR loaded on PhCS are shown in Fig. 7. PhCS has considerable number of heterogeneous pores where there is a perfect possibility for AR to be trapped and adsorbed. The structure of PhCS changed upon AR adsorption and showed a tendency to form agglomerates.

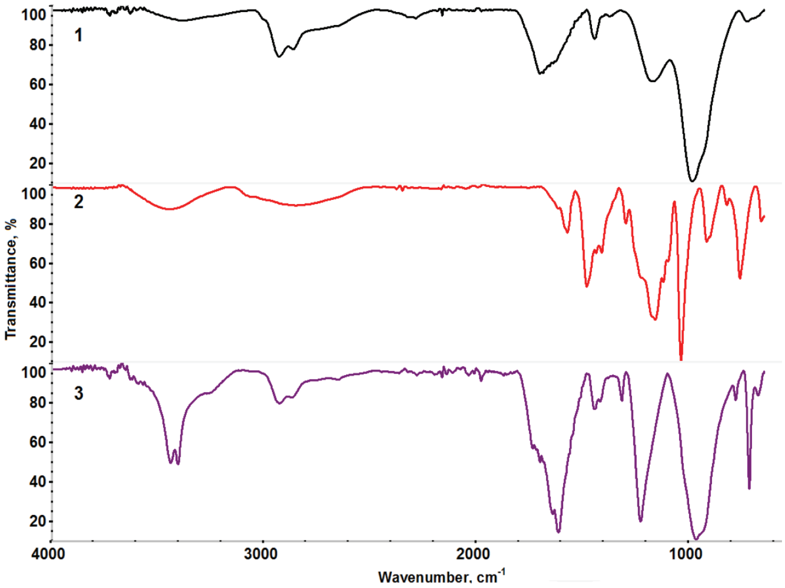

Fig. 6. Normalized FTIR spectra of the sorbent before adsorption (1), pure AR (2) and sorbent after adsorption of AR (3).

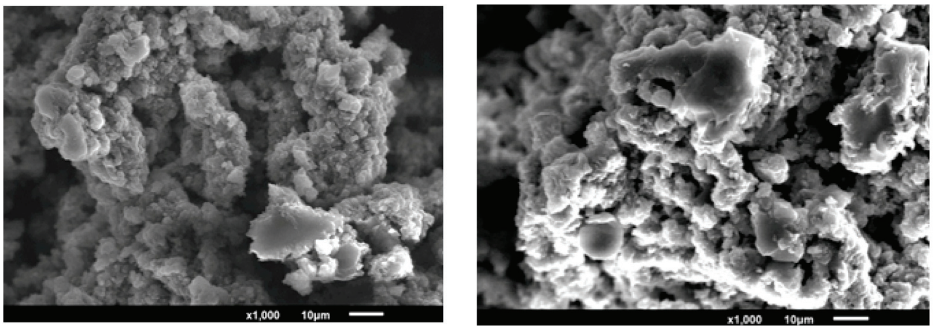

Fig. 7. SEM micrographs of: a) PhCS and (b) AR loaded PhCS (magnification: 1000×).

CONCLUSIONS

In this study, the ability of PhCS, which was synthesized *via* oxidative chlorophosphorylation of butadiene rubber with subsequent hydrolysis, to bind arsenazo III dye was tested using equilibrium, kinetic and thermodynamic aspects. The process equilibrium was expressed by the Langmuir, Freundlich Temkin and Dubinin–Radushkevich models. The equilibrium data were described by the Langmuir model. The thermodynamic parameters obtained from the adsorption constants (K_L) indicated spontaneous nature of the adsorption process. The positive values of $\Delta S^{\ominus}$ showed the increased randomness at the solid/solution interface during adsorption and the positive values of $\Delta H^{\ominus}$ indicated the adsorption process was endothermic. The kinetics of arsenazo III dye adsorption onto phosphorus-containing sorbent was examined using the pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models. The results indicated that the pseudo-second-order equation provided the best correlation of the sorption data.

The experimental results demonstrated that the PhCS can be successfully used for the removal of AR from aqueous solutions.

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ИЗВОД

АДСОРПЦИЈА АРСЕНАЗО (III) БОЈЕ ПОЛИМЕРНИМ СОРБЕНТОМ КОЈИ САДРЖИ ФОСФОР

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Полимерни сорбент који садржи фосфор је коришћен за уклањање арсеназо (III) боје из воде. Испитиван је утицај различитих параметара на адсорпционе карактеристике: pH раствора, полазне концентрације боје, дозе сорбента, времена контакта и температуре. Равнотежни подаци су анализирани применом различитих адсорпционих изотерми: Langmuir, Freundlich, Temkin и Dubinin–Radushkevich. Највећи капацитет за монослојну адсорпцију је добијен на 55 °C (27,75 mg g^{-1}). Израчунати су термодинамички параметри, као што су промене слободне енергије, енталпије и ентропије, и закључено је да при порасту температуре опада адсорпциони капацитет што указује на ендотермну природу процеса. Кинетички параметри су изведени из кинетичких модела (псеудо-првог реда, псеудо-другог реда и интерчестичног). Скенирајућа електронска микроскопија и инфрацрвена спектроскопија са Фуријеовом трансформацијом су коришћене за карактеризацију сорбента и потврду механизма адсорпције.

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