**Adsorption of arsenazo (III) by phosphorus-containing polymer sorbent**

**RASIM M. ALOSMANOV**

*Department of Chemistry, Baku State University, AZ1148, Baku, Z.Khalilov 23, Azerbaijan.*

[*r\_alosmanov@rambler.ru*](mailto:r_alosmanov@rambler.ru)

*Abstract.* Phosphorus-containing polymer sorbent was employed for removal hazardous Arsenazo (III) dye from water. The adsorption characteristics were determined by the study at different parameters such as effect of solution pH, effect of initial dye concentration, sorbent dose, phase contact time, and temperature. The equilibrium data were analyzed on the basis of various adsorption isotherm models, namely Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich. The highest monolayer adsorption capacity has been obtained (24.75 mg g-1) at 55°C. Different thermodynamic parameters such as free energy, enthalpy, and entropy have been calculated and it was concluded that when temperature rises, adsorption increases, indicating the endothermic nature of the process. Kinetic parameters were derived by pseudo-first-order, pseudo-second-order and intraparticle kinetic models. Scanning Electron Microscopy and Fourier Transform Infrared spectroscopy were used to characterize the sorbent and also to validate the adsorption mechanism.

*Keywords:* Dye; Removal; Polymeric sorbent; Equilibrium; Kinetic; Thermodynamics

*Running title*: Adsorption of dye by polymer sorbent

INTRODUCTION

Dyes, generally are a synthetic organic compounds having complex molecular structures and high molecular weight. These properties increase wastewater treatment difficulties. It is commonly-known that the wastewaters with dye are poisonous, carcinogenic and teratogenic to humans. Therefore the efficient disposal of dyestuff in wastewater 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 ion exchange.6 Most of these techniques have significant disadvantages including incomplete dye removal, high reagent and energy necessity, low selectivity, high capital, operational cost and generation 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 a different techniques. As compared to other techniques, adsorption is the superior in simplicity of design, initial cost, ease of operation and intensitivity 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. The characteristic feature is the presence in their structures one or more azo groups, together with hydroxyl groups, amine and substituted amine groups as auxochromes. They have found a broad application in pharmaceutical, cosmetic, food, dyeing/textile industry and analytical chemistry.10 One of representative of azo dyes is Arsenazo (III) (AR, bis-azo derivative of chromotropic acid containing arsenic), which is widely applied for spectrophotometric determination of metal ions and proteins.11-18 AR is a hazardous chemical compound, which may cause a 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 Thus, investigations about removing AR from aqueous medium are an urgent problem, esspetially this informations in literature are presented restricted.20

The aim of this work was to study the efficiency of phosphorus-containing polymer sorbent (PhCS) in the removal AR from aqueous solutions. The studies are carried out involving parameters such as the initial dye solution's concentration, solution pH, sorbent dose, phase contact time, and temperature. Equilibrium, kinetic and thermodynamics analysis were conducted to understand of the adsorption process. To obtain more information about the adsorption mechanism, Scanning Electron Microscopy (SEM) and Infrared Spectroscopy with a Fourier Transform (FTIR) were used.

The synthesis of PhCS by chemical modification (oxidative chlorophosphrylation reaction) of industrial polymer – butadiene rubber (BR) was developed by our group and described previously.21 It was estabilished that this reaction can be performed using readily available commercial reagents under mild condition and in simple equipment.

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 PCl3, CCl4, H2SO4, acetone and O2.21 BR was purchased from Voronezh Synthetic Rubber Manufactory (Russia). PCl3, CCl4, H2SO4 and acetone (p.a.) were purchased from Vecton (Russia) and used without their further purification.

AR ((HO)2C10H2(SO3H)2(N=NC6H4AsO3H2)2) weights 776.4 g mol−1 and has absorbance maximum (λmax) of 530 nm (Fig.1). Ionizable groups have following pKa values:22 pK1 = -2.5; pK2= 0, pK3 and pK4= 2.5; pK5 and pK6 = 5.3; pK7 = 7.5; pK8 = 12.4. K1, and K2 refer to sulfonic acid, K3, K4, K5, and K6 − arsenic acid, and K7, and K8 − hydroxyl groups respectively. The pH of the solution was maintained using HCl and NaOH. AR, HCl and NaOH were of analytical reagent grade chemicals (Gorex Analyt GmbH).

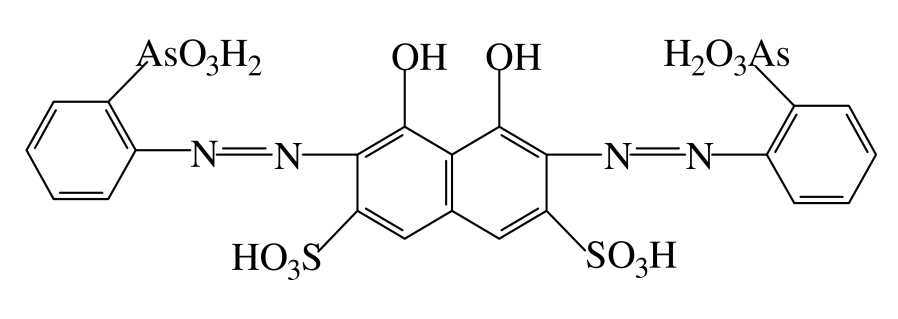


Figure 1.The structure of AR

*Preparation of Phosphorus-containing polymer sorbent21*

A 5 % solution of BR in CCl4 was prepared. After that PCl3 was added to reaction mixture at a ratio of 1:5 (BR:PCl3, w/w) and the reaction system was purged with oxygen, which was supplied to the reaction medium through the concentrated H2SO4 at a rate of 7 L·h-1. The reaction was carried on for 8 hours and after that time completion product of reaction (solid phase, modified BR) was separated from liquid phase (CCl4, POCl3, PCl3). Then modified BR was added to the icy distilled water. Whereupon polymer was separated and carried out the hydrolysis process (50°C for 4 h with continuous stirring). Then final product was filtered, washed with distilled water up to getting neutral pH washed with acetone and dried firstly in the air and then under vacuum, in 40°C.

*Preparation and analysis of AR solutions*

The stock solution of AR was prepared in deionized water (Co=1000 mg L−1). The required concentrations of AR solutions were prepared by appropriate dilutions of the stock solutions. The remaining concentrations of AR were determined by using a double beam UV–Vis spectrophotometer (Specord 210 Plus, Analytikjena) at wavelength of 530 nm.

*Batch adsorption studies*

The influence of the solution pH, sorbent dose, contact time, temperature, and initial concentration were investigated forthe adsorption of AR on the PhCS. For this purpose, at the beginning, preliminary experiments were carried out. An accurately weighed amount of PhCS (0.03-0.60 g) have been placed into bottles and filled up with solutions of AR and pH. Herewith initial concentrations of AR have been changed in the range between 5 and 120 mg L-1. Similar experiments were performed at values of pH 1÷9 and at the temperatures of 25, 35, 45 and 55 °C. For each experiment 100 mL solutions was used. The bottles were shaken in a temperature-controlled shaker (IKA, Germany) for 24 h. After the time, the solutions have been filtrated and the concentration of AR in filtrate has been determined. The adsorption capacity (*q* / mgg-1) and adsorption degree (*R*/ %) has been calculated by the equations (1) and (2):

 (1)

 (2)

where *C*0, *C*e– initial and equilibrium concentration of AR in solution respectively, mgL-1, *V* – solution volume and *m* – sorbent dose (g).

The results revealed that for studying the influence of pH on the adsorption of AR is sufficient carry out experiments by using dye solution with an initial concentration of 60 mg L-1 at a concentration of 3.3 g L-1 adsorbent. The dye solution with similar initial concentration was chosen for studying of impact of the sorbent dose on the adsorption process, wherein the pH of solutions was equal to 1.

The influence of temperature and AR initial concentration upon 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 Temkin25 and Dubinin*-*Radushkevich (D–R)26 models to understand theprocesses governing dye adsorption on the PhCS.The equations of these models are given in formulas (3) – (6):

|  |  |  |
| --- | --- | --- |
| Langmuir isotherm: |  | (3) |
| Freundlich isotherm: |  | (4) |
| Temkin isotherm: |  | (5) |
| D–R isotherm: |  | (6) |

where *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 free energy of adsorption. *K*F and *n* are the Freundlich constants that indicate relative capacity and adsorption intensity, respectively.

In Eq. (5) constant *A* denotes Temkin constant used to examine adsorbate–adsorbate interactions and *B* is the constant related to adsorption heat. In Eq. (6) *q*s is the theoretical isotherm saturation capacity (mg g-1), ** is a constant related to a sorption energy, and *ε* is the Polanyi potential which is related to the equilibrium concentration as follows

** (7)

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

The constant *β* gives the mean free energy, *E*, of sorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using formula

** (8)

Thermodynamic parameters of adsorption were determined using classical thermodynamic equations (9) and (10).27

 (9)

 (10)

where *K* is the distrubition coefficient (L g-1), *ΔH°* / J mol-1and *ΔS*° / J mol-1 K-1 are enthalpy and entropy changes, respectively and *ΔG*° is Gibbs free energy of adsorption.

To identify of contact time effect on the adsorption process, the experiment conditions were chosen based on preliminary experiment (mentioned above): temperature – 25 °C; initial AR conc. − 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 evaluate the kinetics of the adsorption process, pseudo-first-order, pseudo-second-order, and intraparticle diffusion models were employed to interpret the experimental data [Eqs. (11) – (13)].28-30 The pseudo-first-order equation was represented by

 (11)

where *k*1 (min-1) is a rate constant of adsorption, *q*t is the adsorbed amount of ions at time *t* (min), and *q*e denotes the adsorbed amount of ions at equilibrium, both in mg L-1.

The pseudo-second-order equation can be expressed as

 (12)

where *k*2 (g mg-1 min-1) is a rate constant of adsorption of pseudo-second-order.

The intraparticle diffusion equation is expressed as:

 (13)

where *k*i (mg g-1/2 min-1/2) is the intraparticle diffusion rate constant and *C* is the intercept.

The obtained results were statistically processed by standard methods.31,32 The average experimental error was estimated for the value less than 4 %.

*FTIR Spectroscopy*

The FTIR spectra for the sorbent, dye and the dye attached to the sorbent were recorded on Thermo Nicolet iS10 FTIR spectrometer (Thermo Scientific) with ATR equipment (SMART iTX). Samples were analyzed after vacuum drying. The obtained spectra were baseline corrected and normalized using Omnic v9.0 software (Thermo Scientific).

*Scanning Electron Microscopy*

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

RESULTS AND DİSCUSSİON

*Description of the reaction and characterization of the Phosphorus-containing polymer sorbent*

The reaction procedure was described elsewhere in details.21 It was emphasized that during the modification reaction of the polymer cross-linking process occurred between macromolecular chains. As a results we obtained cross-linked products with a different functional groups such as: -P(O)Cl2 (phosphonyldichloride) and -OP(O)Cl2 (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 cross-linked structure was insoluble in organic solvents, mineral acids and alkalis. 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 constant: pKa1, pKa2 | 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 organizers 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 physical 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

Fig. 2 shows the dependence between the pH and the adsorption degrees values of AR. Its easy to notice from Fig. 2, that while the solution pH increased from 1 to 9, *R* decreased from 86.5 % to 25.9 %. The highest values of removal efficiency were obtained in acidic solutions (pH = 1−2) due to the fact that at low pH values (pH<3) functional groups of the PhCS are protonated.34 Moreover molecular complex of a dye is partially ionized due to sulfonic acid groups (pK1 = -2.5, pK2 = 0).22 It causes the adsorption process, that takes place due to the coordination interaction between uncharged (unionized) arsenic acid and hydroxyl groups of the dye with the −P=O groups of the sorbent.

The removal efficiency was decreased at high pH values, due to abundance of OH− ions 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.

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Figure 2. Effect of the solution pH on the AR adsorption by PhCS: Initial AR conc. − 60 mg L−1, PhCS conc. − 3.3 g L−1, contact time − 120 min., temp. –25°C

As it is 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 an equilibrium between a hydroxy azo tautomer and quinone hydrazone tautomer, although the quinone hydrazone tautomer generally dominates. It is possible for AR at high pH values (>7). This provides a partial sorption in this interval of pH solution.

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

*Effect of the sorbent dose to its sorption properties*

Fig. 3 shows the effect of sorbent dose on the adsorption degree. It was observed that the adsorption degree value increased with the increasing sorbent dose until reaching an equilibrium value after 0.33 g (which corresponds to 86.0 % of the initial dye amount adsorbed onto PhCS). An increase in the adsorption degree may be concluded due to the increase in more active functional groups, resulting in the availability of more adsorption sites. Therefore, in the following experiments, the sorbent dose was fixed at 0.33 g.

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Figure 3. Effect of PhCS dose on AR adsorption degree:

Initial AR conc. − 60 mg L−1, contact time − 120 min., temp. –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. Fig. 4 presents the plot of the adsorption degree of AR versus contact time at selection condition (see experimental part). As can be seen from Fig. 4., there was no considerable change of adsorption degree of dye after 60 min.

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Figure 4. Effect of contact time: Co=60 mq L-1, sorbent dose = 0.33 g/100 mL, pH=1

*Effect of initial AR concentration and temperature*

A major factor affecting the distribution of adsorbates between solid and liquid phases is their initial concentration. Besides this investigation of initial concentrations at different temperatures allowed to get additional informations about the mechanism of adsorption process.35 Hence, the influence of the initial concentration on the adsorption was investigated considering the temperature. All results of that study are shown in Table II.

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 is relatively high. The adsorption degree decreases with increasing initial concentration and adsorption capacity of PhCS was larger with increase the dye initial concentration. As seen from the results *q*e stabilized in the higher concentrations. This indicates that PhCS has a limited number ofactive sites for the adsorption, and at lower concentrations, almost all the dye molecules are adsorbed on the surface. However, an increase in the initial AR concentration lead to rapid saturation of sorbent surface. Besides this, with an increase the temperature from 25 to 55 °C causes the adsorption degree and adsorption capacity increase. This result may be caused by an increase of the AR molecules mobility and an increase the number of active sites on the sorbent surface. On the other hand the adsorption process of AR on the PhCS is endothermic in the nature and may involve chemical sorption. Endothermic nature of the adsorption of pollutants have also been reported in other several studies, i.e., sorption of Pb2+ on the cellulose-based sorbent, sphagnum moss peat, the adsorption of Pb2+ on the phosphate-modified kaolinite clay and the sorption of Cu2+ on the tree fern and the adsorption of water-soluble dye reactive brilliant blue KN-R on the functionalized resin.36-39

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

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| C0 /  mg L−1 | 25°C | | 35°C | | 45°C | | 55°C | |
| *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 |

*Equilibrium modelling*

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

The Langmuir model is used to determine the homogeneity of the adsorption process. According to this model, the adsorbent’s surface is homogeneous, each active site on the adsorbent’s surface has the ability to sorb only one adsorbate molecule, and there are no interactions between the adsorbed molecules. In addition, in terms of energy, the active sites are equivalent to each other. The values of Langmuir parameters (*q*max and *K*L, equation (3)) were determined from the linear plots of *C*e/*q*e versus *C*e.

The Freundlich isotherm model involves heterogeneous surface adsorption sites that have different adsorption energies and provides no information about the monolayer adsorption capacity. The Freundlich equation can be linearized by taking logarithms and constants. The values of Freundlich constants (equation (4)), i.e. *K*F and 1/n, were calculated from the linear plots of ln*q*e vs. ln*C*e, respectively.

Temkin isotherm is another adsorption model considering adsorbent–adsorbate interactions. The model assumes that these interactions cause a decrease in the heat of adsorption of molecules in the layer and the binding energies show a uniform distribution in the adsorption process. The values of the *A* and *B* (equation (5)) were determined from plots of *q*e vs. *lnC*e.

The D–R isotherm model is a semi-empirical equation where adsorption follows a pore ﬁlling mechanism. It assumes that the adsorption has a multilayer character, involves Van der Waals forces and is applicable for physical adsorption processes. The values of the **, and *q*s parameters were determined from plots of *lnC*e versus *ε2* (equations (6) and (7)).

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 | Parameters | Temperature, °C | | | |
| 25 | 35 | 45 | 55 |
| Langmuir | *KL*, 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 |
| *r2* | 0.9838±0.0374 | 0.9887±0.0376 | 0.9929±0.0377 | 0.9916±0.0377 |
| Freundlich | *KF* | 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 |
| *r2* | 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 |
| *r2* | 0.9166±0.035 | 0.9147±0.0348 | 0.9364±0.0356 | 0.9580±0.0364 |
| D–R | *qs*, | 12.57±0.48 | 13.20±0.50 | 14.55±0.55 | 17.24±0.66 |
| 107, | 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 |
| *r2* | 0.6225±0.0237 | 0.6362±0.0242 | 0.7204±0.0274 | 0.7815±0.0297 |

For the all four investigated systems, Langmuir isotherm correlated better (*r*2> 0.980) with the experimental data of adsorption equilibrium of AR on PhCS than Freundlich, Temkin and D–R isotherms. The adsorption data of dye in accordance with the Langmuir isotherm shows 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 does 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 accordance with the experimentally obtained values.

The value of *K*F and 1/n at 25°C temperature were 3.471 and 0.5814 respectively, with a correlation coefficient (*r2*) 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 0.5814 shows that 58.14% of the active sites onthe surface of the PhCS had equal energies,40 which by increasing the temperature reduced.

Calculated values of Temkin isotherm constants also confirm chemisorption onto the sorbent (correlation coefficients>0.91).

As seen from the Table III the D–R theoretical monolayer saturation capacity (*q*s) for AR was 12.57 mg g-1 with a correlation coefficient (*r2*) of 0.6225 at 25°C temperature. 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 monolayer surface, whereas in the D–R model it 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 has been found.

The Table III also shows that the value of *E* is between 1 and 4 kJmol-1 the sorption process is a physical adsorption process. But the regression parameter *r2* (0.6÷0.8) showed that this isotherm model did not provided a very good fit to the experimental data.

On the basis of the received data the Langmuir isotherm’s essential characteristics were applied for calculation of 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

** (14)

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

TABLE IV. Comparison of *q*max of PhCS with adsorbents reported in the literature for AR

|  |  |  |
| --- | --- | --- |
| Adsorbent | *q*max, mg g-1 | References |
| Phosphorus-containing polymer sorbent | 24.75 | Present work |
| Activated carbon (AC) | 10.20 | 20 |
| Multiwalled carbon nanotubes (MWCNT) | 30.58 | 20 |

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

*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 *KL* at different temperatures were treated by van't Hoff equation (equation (10). Δ*H*° and Δ*S*° can be determined from the slope and intercept of the plot of *lnK* versus *T*-1 (Fig.5).

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

The values of *ΔH°* and *ΔS°* are reported in Table V. The positive values of *ΔH°* show endothermic nature of adsorption, while positive values of *ΔS*° 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 | Δ*G*° / kJmol-1 | Δ*H*°/ kJmol-1 | Δ*S*°/ Jmol-1K-1 | *T*Δ*S*°/ kJmol-1K-1 | *r2* |
| 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 *ΔG*° values were calculated at different temperatures (equation (10)) and also reported in Table V. The negative values of *ΔG*° indicate that the adsorption reaction occurs spontaneously. The data given in Table V also show a slight change in the values of *TΔS*° at all temperatures and |*ΔH*°|<|*TΔS*°|. This indicates that the adsorption process is dominated by entropy rather than enthalpy changes.

*Kinetic modelling*

Using the appropriate equations (11-13) and plots (data not shown) parameters of three different kinetic models (pseudo-first-order, pseudo-second-order, and intraparticle diffusion models) were calculated, which 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 | | |
| *k1*/ min-1 | *q*1/ mg⋅g-1 | *r2* | *k2*/ g mg-1 min-1 | *q*1/ mg g-1 | *r2* | *k*i/ mg g-1 min-1/2 | *C* | *r*2 |
| 0.084  ±0.003 | 23.808  ±0.905 | 0.9562±0.0363 | (1.663±0.063)·  10-3 | 23.810  ±0.905 | 0.9773  ±0.0371 | 1.418  ±0.054 | 5.809  ±0.221 | 0.9353  ±0.0356 |

Based on the correlation coefficients, the equation of the pseudo-second-order model was that contributed the most suitable for the experimental kinetic data, suggesting the chemical sorption as the rate-limiting step of the mechanism of adsorption without involvement of a mass transfer in solution.28-30

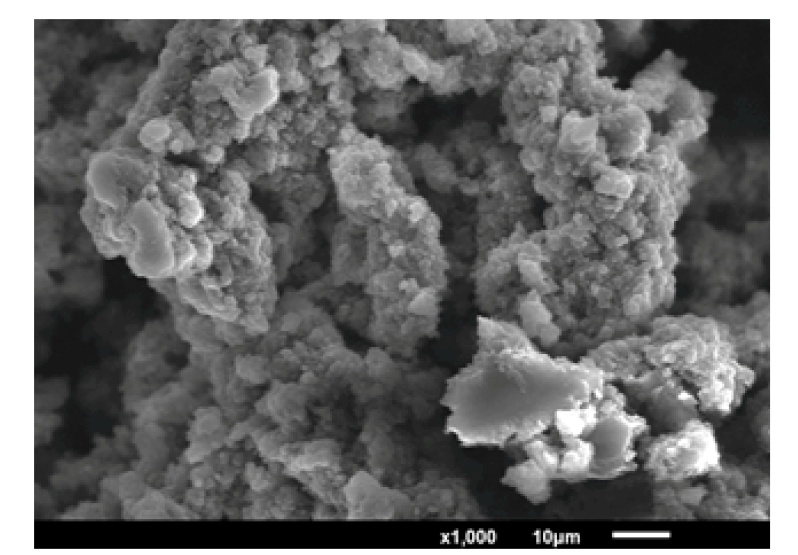
*FTIR Spectroscopy and SEM studies*

In accordance with other literature information about structural characterization of the polymers (sorbents, resins) before and after dyes adsorption was performed by FTIR spectroscopy and SEM analysis.43,44 The FTIR measurements show (Fig. 6) the presence of following groups for PhCS (Spectrum 1, before adsorption): O−H (3343 cm-1; stretch vibration), C−H aliphatic (2978 cm-1; 2935 cm-1 stretch vibration), O−H in P−O−H (2862 cm-1, 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. After AR adsorption (Spectrum 3), the changes occurred mainly in the P=O and P–OH groups. Signals for those groups are 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 involves mainly P=O and P–OH groups. All of these alterations were a clear indication of interactions that took place between AR and the PhCS.

D:\Rasim\Öz məqalələrim\Üzərində işlədiyim məqalə və s\Tək məqalələr\Arsenazo III\Journal of the Serbian Chemical Society\Figure 6. Newest.tif

Figure 6. Normalized FTIR spectra of the sorbent (1-before adsorption, 3-after adsorption) and dye (2)

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



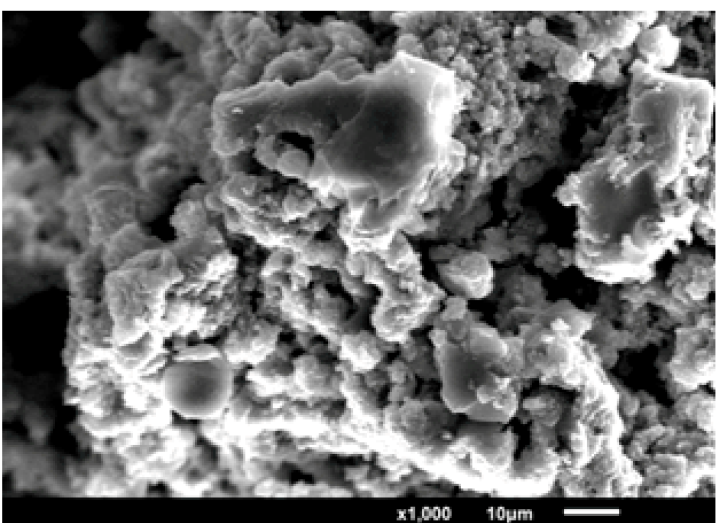


Figure 7. SEM of (a) PhCS and (b) AR loaded PhCS (magnification: x1000)

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 wastested 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 adsorption process. The positive values of *ΔS*° showed the increased randomness at the solid–solution interface during adsorption and the positive values of *ΔH*° 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 PhCS can be successfully used for the removal of AR from aqueous solutions.

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