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RESEARCH INTO SORPTION CONDITIONS OF 2-(4-SULFOPHENYL AZO)-1-AMINO-8-HYDROXYNAPHTHALENE-3,6-DISULFONIC ACID BY COMMERCIAL ANION EXCHANGER AB-17

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Abstract: To obtain a new modified sorbent, the conditions for maximum sorption of the chelate reagent 2-(4-sulfophenylazo)-1-amino-8-hydroxynaphthalene-3,6-disulfonic acid (SPAAHS) by a strongly basic AB-17 anion exchanger were selected. The conditions for modifying the anion exchanger were studied by spectrophotometric analysis on a Specord 210 Plus spectrophotometer from Analytik Jena. The influence of such factors as the acidity of the solution, the contact time of the sorbed reagent, and the concentration of SPAAHS on the sorption process was analyzed. According to the saturation curves, the static capacity of the anion exchange resin for the sorbed reagent was established. Also, the description of the adsorption isotherm of SPAAHS with the AB-17 anion exchanger was performed using the models of Langmuir, Freundlich, Temkin and Redlich-Peterson. To calculate the value of the ABERage free energy of adsorption, the adsorption isotherm of SPAAHS with the AB-17 anion exchanger was processed using the Dubinin-Radushkevich model. On the basis of the results obtained, conclusions were made about the nature of the bond between the anion exchanger and the sorbed reagent. To prove the proposed mechanism of sorption of SPAAHS by the AB-17 anion exchanger by the density of functional theory (DFT) method, using the Orca 4.2.0 program, an estimated quantum-chemical calculation of the dissociation energies of various acidic functional groups according to which an exchange reaction is possible on the anion exchanger AB-17.

Keywords: sorption, AB-17 anion exchanger, p-sulfobenzene-azo-As acid, modified sorbent, isotherm models, quantum-chemical calculations, adsorption mechanism.

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Introduction

The state of the environment is the most important factor for mankind and society to exist. The problem of soil and water pollution with toxic substances, industrial and household waste is becoming the main cause of environmental destruction in the modern world.

Synthetic dyes are one of the classes of toxic compounds that have a serious impact on the environment [1]. Industrial wastewater containing synthetic dyes when released into the environment leads to a decrease in the penetration of daylight into the water column, which in turn affects the natural biochemical processes occurring in water bodies [2]. In addition, the ingress of synthetic dyes on biological treatment facilities leads to the decrease in the efficiency of biological treatment due to sorption on the surface of suspended particles of activated sludge [3]. The aromatic structure of synthetic dyes makes them resistant to biological oxidation. Synthetic dyes can be conditionally divided into anionic, cationic, nonionic, etc. Cationic dyes are more toxic than anionic ones [4].

Obtaining new selective sorbents for wastewater treatment is an urgent task of modern chemistry and chemical ecology, since the scale of production is constantly expanding and the requirements for water quality are growing [5]. Modern sorbents are used both for
the sorption of organic reagents [6–9] and for purification from toxic metal ions [10–13]. A large number of studies deal with the removal of synthetic dyes [14–17]. Various materials were used as adsorbents to remove dyes, such as silica gel [18–20], activated carbons [21–23], magnetic materials based on iron compounds [24], metal hydroxides [25], and other mesoporous materials [26]. The search for regenerated sorption materials for the removal of dyes from aqueous solutions is an urgent problem. At the same time, the regenerated sorbent can be used for subsequent cycles of removing dyes from aqueous solutions. In this case, the selective extraction of cationic dyes will allow them to be returned to the dyeing bath. In this regard, in this work, we studied the sorption of a model compound 2-(4-sulfophenylazo)-1-amino-8-hydroxynaphthalene-3,6-disulfonic acid (SPAAHS) which has the properties of cationic dyes, on a commercially available AB-17 anion exchanger.

**Experimental**

**Reagents and equipment.** The strongly basic anionite AB-17 in the OH form was chosen as the sorbent. A dye solution with a concentration of $1 \times 10^{-3} \text{ M}$ was prepared by dissolving its exact weight in distilled water alkalized with a 1 M sodium hydroxide solution.

To create a certain pH value in the systems under study, 0.1 M solutions of HCl and NaOH were used. The pH values of the studied solutions were monitored using a pH-150MI universal ion meter and the mass of substances was measured on an HTR-220CE analytical balance.

**Studies of the effect of pH.** Solutions with pH values from 1.0 to 12.0, containing 2.0 ml of SPAAHS solution with a concentration of $1 \times 10^{-3} \text{ M}$ and 0.025 g of AB-17 anion exchanger, were prepared in 100 ml bottles.

The resulting system was stirred on a mechanical stirrer for an hour at a temperature of 20±2°C. Then it was filtered through a “white ribbon” filter, rinsing with distilled water. The filtrate and washing water were collected in volumetric flasks with a capacity of 50 ml, the volume of the solution was brought up to the mark with distilled water, the pH was checked, and the amount of the unsorbed component was determined on a spectrophotometer. The degree of sorption (R, %) was calculated by the formula:

$$R = \frac{n_{\text{ini}} - n_{\text{res}}}{n_{\text{ini}}} \times 100 \%,$$

where $n_{\text{ini}}$ is the initial amount of the dye, mmol; $n_{\text{res}}$ is the amount of dye after sorption, mmol.

**Research into the effect of duration to phase contact.** The study of the dependence of the degree of sorption on the duration of phase contact was carried out in the range from 5 to 120 min. For this purpose, a series of solutions were prepared containing 2.0 ml of the reagent with a concentration of $1 \times 10^{-3} \text{ M}$ and 0.025 g of the AB-17 anion exchanger, and the optimal pH value was set. The solutions were then filtered through a white ribbon filter, the amount of the unsorbed component determined on a spectrophotometer, and the degree of sorption was calculated using formula (1). Based on the data obtained, a plot of the dependence of the degree of sorption of the reagent on the duration of the contact of the phases was built, from which the time of sorption of the maximum amount of the reagent was determined.

**Studies of the effect of dye concentration.** To plot the sorption isotherm of SPAAHS with an AB-17 anion exchanger, a series of solutions with a sorbent mass of 0.025 g and an increasing content of SPAAHS (2.5; 5.0; 7.5; 10.0; 12.5; 15.0; 17.5; 20.0 ml with an initial concentration of $1 \times 10^{-3} \text{ M}$) at optimal pH values and phase contact time.

After the sorption of time, the amount of the unsorbed reagent was determined by the spectrophotometric method, and a plot of the dependence of the amount of the sorbed reagent (a, mmol/g) on the equilibrium concentration ($C_{eq}$, mmol/l) was plotted. The sorption value (a, mmol/g) was found by the formula:
where $n_{\text{ini}}$ is the initial amount of the dye, mmol; $n_{\text{res}}$ is the amount of dye after sorption, mmol; $m_s$ is the mass of the sorbent, g.

**Establishment of the probable sorption mechanism.** To elucidate the mechanism of chemisorption of SPAAHS on the AB-17 anion exchanger by the density functional theory (DFT) method [27], using the Gaussian 09W program, an estimated quantum-chemical calculation of the dissociation energies of various acidic functional groups, according to which the exchange reaction on the AV-17 anion exchanger is possible with release of HCl. The geometric optimization of the molecule under study was carried out at the level of the B3LYP/6-311++g(d,p) theory with a minimum spin multiplicity and taking into account the influence of the aqueous medium at the level of the CPCM model theory [28].

The dissociation energy was calculated by the formula:

$$ E_{\text{dis}} = E_{Ac^-} + E_{H^+} - E_{HAc} $$

where $E_{HAc}$ is the total energy of the studied acid molecule in the aquatic environment, $E_{Ac^-}$ is the total energy of the anion of the acid residue of the studied acid molecule in an aqueous medium, $E_{H^+}$ is the energy of the H+ cation in an aqueous medium.

**Results and discussion**

**Effect of pH.** The acidity of the medium is one of the main factors influencing the degree of the reaction of SPAAHS with the AB-17 anion exchanger. The results of the study of the dependence of the degree of sorption of SPAAHS on the pH of the solution are shown in fig. 1. The results of the experiment showed that the maximum degree of sorption of the reagent is observed at pH equal to 9.0. At a given pH value, all sulfo groups of the reagent are in a deprotonated state.

**Fig. 1.** Effect of the solution pH to the degree of sorption of SPAAHS on the AB-17 anion exchanger ($m_s = 0.025$ g, $V=2.0$ ml, $C_{\text{reag}} = 1 \times 10^{-3}$M)

**Effect of phase contact duration.** The results of the study carried out at the selected value of the acidity of the medium are shown in Fig. 2. It was established that the most complete sorption of the reagent occurs after 90 minutes of shaking when no value of the sorption degree practically changes.
Fig. 2. Effect of the duration of phase contact to the degree of sorption of SPAAHS on the anion exchanger AB-17 on (mₜ= 0.025 г, V=2.0 ml, Cₜₑₐₑ = 1×10⁻³M, pH=9.0)

Isotherm analysis. The sorption isotherm of SPAAHS with the AB-17 anion exchanger is shown in Fig.3. The statistical capacity of the anion exchanger AB-17 for SPAAHS, found by extrapolation directly to the y-axis from the surface of the plateau of the adsorption isotherm, was 0.155 mmol/g. Given the large size of the molecules of the sorbed reagent, the sorbent under study is characterized by good capacitance capabilities.

Fig. 3. Sorption isotherm of SPAAHS with AB-17 anion exchanger (mₜₑₒ₉= 0.025 г, pH = 9.0, τ = 90 min)

As is evident from Fig. 3, a low percentage of the reagent adsorption is observed in the initial section of the isotherm. This indicates a strong intermolecular interaction of the adsorbate.

To describe the obtained isotherm, the models of Langmuir, Freundlich, Temkin, and Redlich-Peterson described by the following adsorption equations, were used:

\[ a = \frac{a_{\text{max}} \cdot K_L \cdot C_{eq}}{1 + K_L \cdot C_{eq}} \] is the Langmuir adsorption equation \[29\] \quad (4),

\[ a = K_F \cdot \left( \frac{1}{C_{eq}} \right) \] is the Freundlich adsorption equation \[30\] \quad (5),

\[ a = \frac{1}{\alpha} \cdot \ln(K_T \cdot C_{eq}) \] is the Temkin adsorption equation \[31\] \quad (6),
\[ a = \frac{K_R \cdot C_{eq}}{1 + \alpha \cdot C_{eq}} \] is the Redlich-Peterson adsorption equation [32] \hspace{1cm} (7),

To calculate the constants, the linear forms of the following form: adsorption equations were transformed into their

\[ \frac{C_{eq}}{a} = \frac{1}{a_{max} \cdot K_L} + \frac{1}{a_{max}} \cdot C_{eq} \] is the Langmuir adsorption equation \hspace{1cm} (8),

\[ \log a = \log K_F + \frac{1}{n} \cdot \log C_{eq} \] is the Freindlich adsorption equation \hspace{1cm} (9),

\[ a = \frac{1}{a} \cdot \ln K_F + \frac{1}{n} \cdot \ln C_{eq} \] is the Temkin adsorption equation \hspace{1cm} (10),

\[ \log \left( \frac{K_R \cdot C_{eq}}{a} - 1 \right) = \log \alpha + \beta \cdot \log C_{eq} \] is the Redlich-Peterson adsorption equation \hspace{1cm} (11).

As distinct from other adsorption equations containing two constants each, the Redlich-Peterson adsorption equation contains three constants. Therefore, it is not possible to use its linear form to calculate the values of the constants. To solve this problem, we applied the minimization procedure given in [31]. Proceeding from the experimental data on the adsorption values \(a\) and the corresponding equilibrium concentrations of the adsorbate \(C_{eq}\), values of the parameters \(K_R, \alpha\) and \(\beta\) were empirically selected so that the difference between the right and left parts of the linear equation (11) was minimal. Empirically, the value of \(K_R\) is chosen, so that the condition

\[ \log \left( \frac{K_R \cdot C_{eq}}{a} - 1 \right) = \log \alpha + \beta \cdot \log C_{eq} = 0.36. \] Using the \(K_R\) value, a dependency graph was built from \(\log C_{eq}\) and calculated the real values of the constants \(K_R, \alpha\) and \(\beta\).

To calculate the constants of the equations, graphical dependencies are built as follows:

\[ \frac{C_{eq}}{a} \] from \(C_{eq}\) is for the Langmuir adsorption equation,

\[ \log a \] from \(\log C_{eq}\) is for the Freindlich adsorption equation,

\[ a \] from \(\ln C_{eq}\) is for the Temkin adsorption equation,

\[ \log \left( \frac{K_R \cdot C_{eq}}{a} - 1 \right) \] from \(\log C_{eq}\) is for the Redlich-Peterson adsorption equation.

The constants of the corresponding equations were calculated from the section cut off on the y-axis and from the tangent of the slope angle.

The constants of all used models are summarized and shown in Table 1.

<table>
<thead>
<tr>
<th>№</th>
<th>Model type</th>
<th>Model parameters</th>
<th>Model parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Langmuir</td>
<td>(K_L, \text{l/mmol})</td>
<td>(a_{max}, \text{mmol/g})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.119</td>
<td>0.22</td>
</tr>
<tr>
<td>2</td>
<td>Freindlich</td>
<td>(K_F, (\text{mmol/g}) \cdot (\text{l/mmol})^{1/n})</td>
<td>(n)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.848</td>
<td>1.741</td>
</tr>
</tbody>
</table>
In terms of applicability for the description of the adsorption process of SPAAHS with the AB-17 anion exchanger, the considered adsorption models can be arranged in the following order:

<table>
<thead>
<tr>
<th>Model</th>
<th>Langmuir</th>
<th>Freundlich</th>
<th>Temkin</th>
<th>Redlich-Peterson</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R^2$</td>
<td>0.9135</td>
<td>0.9122</td>
<td>0.89146</td>
<td>0.8189</td>
</tr>
</tbody>
</table>

From the results of the experiment, it can be seen that the most suitable model is the Langmuir model. This indicates that a monomolecular adsorbate layer is formed on the surface of the sorbent, and all active centers have equal energy and enthalpy.

The mechanism of the adsorption process. The Langmuir, Freundlich, Temkin and Redlich-Peterson models which are analyzed in this paper, despite their wide application, do not provide information about the adsorption mechanism. To establish the proposed mechanism of adsorption, we applied computational and experimental methods. To obtain data on the mechanism of the adsorption process, the equilibrium data were processed using the Dubinin-Radushkevich isotherm model [33]. The Dubinin-Radushkevich equation has the form

$$ a = \frac{0.22 \cdot C_{eq}}{1 + 8.119 \cdot C_{eq}} $$

- the Langmuir equation

Taking into account the calculated adsorption constants, the following adsorption equations for SPAAHS with the AB-17 anion exchanger are proposed:

$$ a = a_{max} \cdot \exp(-k \cdot \varepsilon^2) $$

where

$$ \varepsilon = RT \cdot \ln \left(1 + \frac{1}{C_{eq}}\right) $$

Taking the logarithm of expression (14), we obtained a linear form of the following form

$$ \ln a = \ln a_{max} - k \cdot \varepsilon^2 $$

(15) and built a dependency graph in coordinates $\ln a$ from $\varepsilon^2$. The results are shown in fig. 4.

The results are summarized in Table. 2.
Table 2. Equation constants of the models describing the adsorption of SPAAHS with the AB-17 anion exchanger

<table>
<thead>
<tr>
<th>Dubinin-Radushkevich model</th>
<th>K, mol²/kJ²</th>
<th>a_max, mmol/g</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.0041</td>
<td>0.74</td>
<td>0.897</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 4. Dubinin-Radushkevich adsorption isotherm for the constants calculation.

Fig. 5. Optimized structure, atomic charges (numbers in the center of atoms) and lengths of various chemical bonds (numbers between atoms) of the SPAAHS molecule.

The Dubinin-Radushkevich model is applicable for calculating the average free energy of adsorption according to equation $E = (-2 \cdot K)^{0.5}$ (16) which indicates the nature of adsorption on the adsorbent. The calculated value of $E$, equal to 11.04 kJ/mol indicates that the adsorption process of SPAAHS with the AB-17 anion exchanger...
proceeds with the formation of stable ionic bonds.

Fig. 5 shows the structure of the optimized SPAAHS molecule, the distribution of charges on atoms, and the lengths of various chemical bonds according to the data of the B97-3c method, without taking into account the influence of the aqueous medium. Also, in Fig. 5, the numbers 1, 2, 3, and 4 indicate the possible directions of exchange reactions on the surface of the AB-17 anion exchanger with the release of HCl.

Table 3 is illustrative of the calculated total energies of the SPAAHS molecule (HAc) and its acidic residues (Ac\textsuperscript{−}, Ac\textsuperscript{2−}, Ac\textsuperscript{3−} and Ac\textsuperscript{4−}) formed upon elimination of the H\textsuperscript{+} cation from various functional groups indicated in Fig. 5 numbers 1, 2, 3 and 4, respectively. The last column of this Table shows the dissociation energies of various acidic functional groups calculated by formula (3).

### Table 3. Total calculated energies of reactants and dissociation reactions

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Total energy, Eh*</th>
<th>Reaction</th>
<th>Dissociation energy, Eh</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAc</td>
<td>-2727.625</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Ac\textsuperscript{−}</td>
<td>-2727.103</td>
<td>HAc → Ac\textsuperscript{−} + H\textsuperscript{+}</td>
<td>0.522</td>
</tr>
<tr>
<td>Ac\textsuperscript{2−}</td>
<td>-2727.126</td>
<td>HAc → Ac\textsuperscript{2−} + H\textsuperscript{+}</td>
<td>0.499</td>
</tr>
<tr>
<td>Ac\textsuperscript{3−}</td>
<td>-2727.094</td>
<td>HAc → Ac\textsuperscript{3−} + H\textsuperscript{+}</td>
<td>0.531</td>
</tr>
<tr>
<td>Ac\textsuperscript{4−}</td>
<td>-2727.076</td>
<td>HAc → Ac\textsuperscript{4−} + H\textsuperscript{+}</td>
<td>0.549</td>
</tr>
<tr>
<td>H\textsuperscript{+}</td>
<td>0.0</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

* Eh – atomic unit of energy (Hartree energy)

As can be seen from fig. 5, the optimized structure of the SPAAHS molecule, which has a minimum energy, has the structure of an internal salt with a spatial charge separation (−SO\textsubscript{3}− and −N+H−) at the sulfo group indicated by the number 4. This indicates that this direction is the most probable in the formation of chemical bonds with the AB-17 anion exchanger as a result of the chemisorption exchange reaction (especially at high pH). The next likely direction based on the data in Table 3 is a phenolic hydroxyl group denoted by the number 2, because its dissociation proceeds with the least energy absorption. The rest of the directions are relatively unlikely.

### Conclusion

The quantitative characteristics of the sorption of SPAAHS by the AB-17 sorbent were determined. It was established that the maximum degree of the reagent sorption is observed in the pH range of 9.0 after 90 minutes of shaking. The statistical capacity for the reagent was 0.155 mmol/g. It is shown that the Langmuir model is the most suitable model for describing the process of SPAAHS adsorption with the AB-17 anion exchanger which indicates that a monomolecular adsorbate layer is formed on the sorbent surface, and all active centers have equal energy and enthalpy. The calculated value of $E$, equal to 11.04 kJ/mol indicates that the adsorption of SPAAHS with the AB-17 anion exchanger occurs due to the formation of stable ionic bonds. Based on the results of quantum chemical calculations, the most probable mechanism of chemisorption on the AB-17 anion exchanger is reactions at the sulfo group 4 and the phenolic hydroxyl group 2 of the SPAAHS molecule.


ИЗУЧЕНИЕ УСЛОВИЙ СОРБЦИИ П-СУЛЬФОБЕНЗОЛ-АЗО-АШ КИСЛОТЫ НА АНИОНИТЕ АВ-17

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Аннотация: С целью получения нового модифицированного сорбента подобраны условия максимальной сорбции хелатного реагента п-сульфобензол-азо-Аш кислот (п-СБААК) сильноосновным анионитом АВ-17. Условия модифицирования анионита изучали спектрофотометрическим методом анализа на спектрофотометре Specord 210 Plus фирмы «Analytik Jena». Исследовано влияние кислотности раствора, времени контакта, концентрации п-СБААК на процесс сорбции. По кривым насыщения установлена статическая емкость анионита по сорбируемому реагенту. Описание изотермы адсорбции п-СБААК анионитом АВ-17 осуществлено с применением моделей Ленгмюра, Фрейндлиха, Темкина и Редлиха - Петерсона. Для расчета значения средней свободной энергии адсорбции изотерма адсорбции п-СБААК анионитом АВ-17 обработана с помощью модели Дубинина - Радушкевича. На основе полученных результатов сделаны выводы о природе связи между анионитом и сорбируемым реагентом. Для доказательства предполагаемого механизма сорбции п-СБААК анионитом АВ-17 методом теории функционала плотности (DFT) с помощью программы Orca 4.2.0 проведен оценочный квантово-химический расчет энергий диссоциации различных кислотных функциональных групп, по которым возможна обменная реакция на анионите АВ-17.

Ключевые слова: сорбция, анионит АВ-17, п-сульфобензол-азо-Аш кислота, модифицированный сорбент, модели изотерм, квантово-химические расчеты, механизм адсорбции.

2-(4-SULFOFENİLAZO)-1-AMIİNO-8-HİDROKSİNAFTALİN-3,6-DİSULFO TURŞUSUNUN AB-17 ANİONİTDƏ SORBSİYA ŞƏRAİTİİNİN TƏDQİQİ

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