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ADSORPTION OF OLEIC ACID ON AV-17-8 ANION EXCHANGE RESIN

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Adsorption of oleic acid on AV-17-8 anion exchange resin from a sunflower oil solution is studied. It has been established that preliminary drying of the adsorbent accelerates the completion of the oleic acid equilibrium concentration and increases the acid adsorption degree. An increase in the adsorbent amount enhances the degree of oleic acid adsorption over the entire temperature range studied. An increase in temperature also raises the degree of oleic acid adsorption when using both air-dry anion exchange resin and pre-dried adsorbent. The experimental results are analyzed using Langmuir, Freundlich, and Dubinin-Radushkevich adsorption models. The oleic acid adsorption is satisfactorily described by the Langmuir adsorption equation. According to the values of the adsorption constant calculated by the Freundlich model, it is established that the adsorption of oleic acid on an anion exchange resin is physical. This conclusion is confirmed by the value of the mean adsorption energy calculated using the Dubinin-Radushkevich adsorption model. The thermodynamic parameters of the oleic acid adsorption on AV-17-8 anion exchange resin also are determined. The negative values of the Gibbs free energy and positive value of the adsorption entropy indicate that the oleic acid adsorption on AV-17-8 anion exchange resin occurs spontaneously.

Keywords: adsorption, oleic acid, sunflower oil, AV-17-8 anion exchange resin, Langmuir model, Freundlich model, Dubinin-Radushkevich model.

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Introduction

The transesterification of triglycerides has a significant role in industrial organic chemistry. This process formed esters of higher fatty acids and methyl and 2-propyl alcohol, sucrose, etc. Methyl esters of higher fatty acids are used as biodiesel and intermediates of alkanolamides, higher fatty alcohol synthesis, etc. Currently, sodium or potassium hydroxides or methylates are used as industrial catalysts for triglyceride transesterification with aliphatic alcohols [1]. The advantages of these catalysts are high reaction rate and mild reaction conditions. However, sodium or potassium hydroxides or methylates significantly lose catalytic activity subject to above 0.5 and 1% water and free fatty acids content in vegetable oils, respectively. Such restrictions significantly narrow the range of feedstocks for triglyceride transesterification.

These shortcomings are eliminated by using acid catalysts, which are less sensitive to the high content of free fatty acids in vegetable oils and can catalyze their esterification [2,3]. The process proceeds in one or two stages when using acid catalysts. The first method involves the transesterification of triglycerides with simultaneous esterification of free acids. The second method is the esterification of free fatty acids catalyzed by acid and the transesterification of triglycerides catalyzed by base. The main disadvantage of acid catalysts is their low activity in the transesterification reaction and long reaction time.

Heterogeneous basic or acidic catalysis is another method of transesterification oils with a high content of free fatty acids [4–6]. Such substances catalyze the transesterification of oils containing free fatty acids. The heterogeneous basic or acidic catalysts also have the advantage of being easily separated from the reaction mixture and reused.

A raw materials pretreatment is also offered for oil transesterification containing free fatty acids. This treatment involves removing free fatty acids from the feedstock. Anion exchange resins, zeolites, etc. are effective adsorbents for free fatty acids removal [7,8]. Simultaneously, such purified oils are the appropriate raw materials for transesterification with alcohols catalyzed by sodium or potassium hydroxides or methylates. The free fatty acids adsorption from oils also permits to use of such promising raw materials for transesterification as unrefined or used oils [9,10].

The aim of this study was to investigate the kinetic and thermodynamic of adsorption of oleic acid added to sunflower oil on AV-17-8 anion exchange resin.

Experimental

Oleic acid (DSTU 4830:2007, grade B) and refined sunflower oil (DSTU 4492:2017) were used as raw materials. The AV-17-8 anion exchange resin (top grade) was used as an adsorbent. Refined sunflower oil containing added oleic acid was used as a model solution. The acid number of the solution was 8.5 mg KOH/g. That corresponded to an oleic acid content of 4.3 wt.%. The AV-17-8 anion exchange resin was used as an air-dry substance with 17.5% moisture content. The dried anion exchange resin was obtained at a temperature of 363–368 K.

The oleic acid adsorption from a sunflower oil model solution was studied in a chemical beaker in the temperature range of 303–343 K using a magnetic stirrer. The adsorbent content was varied in the range of 2–6 wt.%. Samples were periodically taken to determine the oleic acid content by acid-base titration according to the method given in Internet resource Biocyclopedia.com[1].

The concentration of oleic acid in sunflower oil solution (mg/g) was calculated by the following formula:

$$C_i = \frac{V_{NaOH} C_{NaOH} M_{OA}}{m}, \qquad (1)$$

where V_{NaOH} is the volume of an alkali solution used to titrate the sample, cm^3; C_{NaOH} is the concentration of the alkali solution, mol/dm^3, M_{OA} is the molar mass of oleic acid, g/mol; and m is the sample weight, g.

The oleic acid amount adsorbed on 1 g of the anion exchange resin was calculated by the following formula:

$$q = \frac{(C_0 - C_i) m_m}{m_{ads}}, \qquad (2)$$

where C_0 is the initial concentration of oleic acid in the sunflower oil solution, mg/g; m_m is the weight of the solution, g; and m_{ads} is the adsorbent weight, g.

The degree (wt.%) of oleic acid adsorption (oleic acid percentage extracted from the sunflower oil solution) was calculated by the following formula:

$$x = \frac{C_0 - C_i}{C_0}. \qquad (3)$$

Results and discussion

The parameters of oleic acid adsorption from sunflower oil were investigated as functions of temperature, adsorbent content in solution, and moisture content in anion exchange resin.

The oleic acid equilibrium concentration in solution is achieved more slowly when using air-dry AV-17-8 anion exchange resin, than when the pre-dried resin is used as an adsorbent (Fig. 1). At 303 K, the equilibrium concentration of oleic acid during adsorption on the dried AV-17-8 anion exchange resin is achieved in about 60 minutes. The equilibrium is 30 minutes faster than when an air-dry anion exchange resin is used as an adsorbent. At 323 K, the equilibrium concentration of oleic acid in solution is reached 60 minutes faster. With a further increase in the adsorption temperature to 343 K, the equilibrium concentration of oleic acid is also reached 30 minutes faster when a pre-dried anion exchange resin is used. When an air-dry anion exchange resin is used, a higher value of the equilibrium concentration of oleic acid is also observed compared to the equilibrium concentration of the acid during adsorption on pre-dried adsorbent in the entire temperature range studied. The degree of oleic acid adsorption when an air-dry anion exchange resin is used is 5–24%, and when a pre-dried adsorbent is used, it is 6–30%. We assume that water increases the oleophobicity of the adsorbent surface and complicates the oleic acid adsorption on anion exchange resin.

An increase in the adsorbent amount naturally results in a lower equilibrium concentration of oleic acid in solution over the entire temperature range studied, regardless of the moisture of the anion exchange resin (Fig. 1).

[1] Biocyclopedia.com. Plant Lab Protocols / Methodology for Lipids. Estimation of free fatty acids. Retrieved April 04, 2024, from https://biocyclopedia.com/index/plant_protocols/lipids/Estimation_of_free_fatty_acids.php.

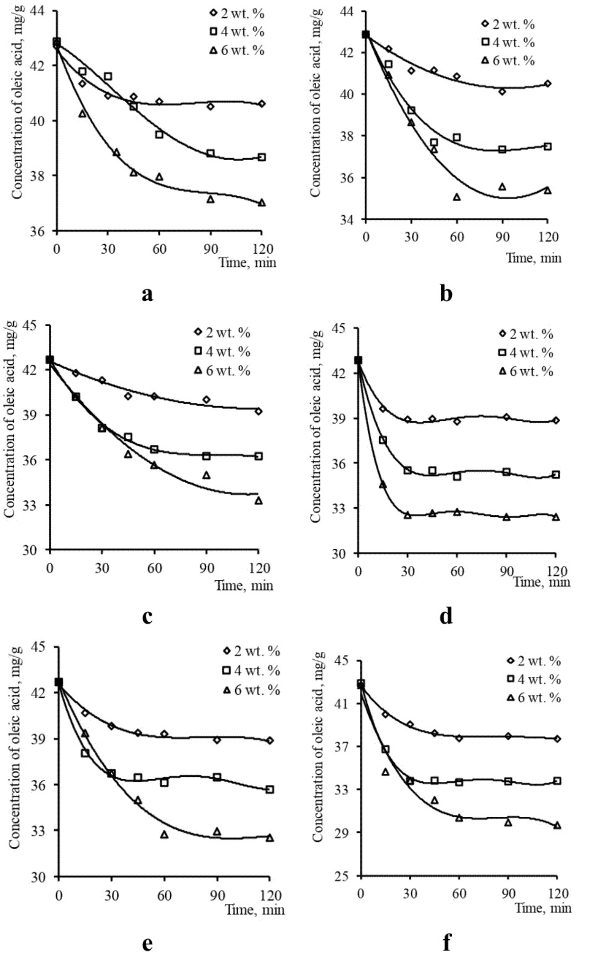


Fig. 1. Kinetics of oleic acid adsorption on air-dry (a, c, e) and pre-dried (b, d, f) AV-17-8 anion exchange resin. Adsorption temperature: a and b – 303 K; c and d – 323 K; e and f – 343 K

An increase in the adsorption temperature slightly reduces the equilibrium concentration of oleic acid (Fig. 1). At a content of air-dry adsorbent in a solution of 2 wt.%, an increase in the adsorption temperature from 303 K to 343 K reduces the oleic acid equilibrium concentration in solution from 40.6 mg/g to 38.9 mg/g. With an increase in the adsorbent content to 6 wt.%, the oleic acid equilibrium concentration decreases from 37.0 mg/g to 32.5 mg/g when the adsorption temperature increases from 303 K to 343 K. Similar results were obtained when using pre-dried AV-17-8 anion exchange resin as an adsorbent (Fig. 1).

The adsorption kinetic curves were processed using the Langmuir, Freundlich, and Dubinin-Radushkevich adsorption models.

The linear form of the Langmuir adsorption isotherm can be written as follows:

$$\frac{1}{q_e}=\frac{1}{q_m}+\frac{1}{bq_mC_e}, \qquad (4)$$

where q_m is the maximum adsorption capacity, mg/g; C_e is the equilibrium concentration of oleic acid in solution, mg/g; and b is the Langmuir constant, g/mg.

The values of K_L were calculated from the Langmuir constant, obtained from Fig. 2. The initial concentration of oleic acid in solution C_0 was determined for the range of 0.0006–0.0008 for air-dry and 0.0009–0.0015 for pre-dried adsorbent in the studied temperature interval according to the following formula:

$$K_L=\frac{1}{1+bC_0}. \qquad (5)$$

Since the K_L values were in the range of 0–1, it can be argued that the oleic acid adsorption on an anion exchange resin is satisfactorily described by the Langmuir equation.

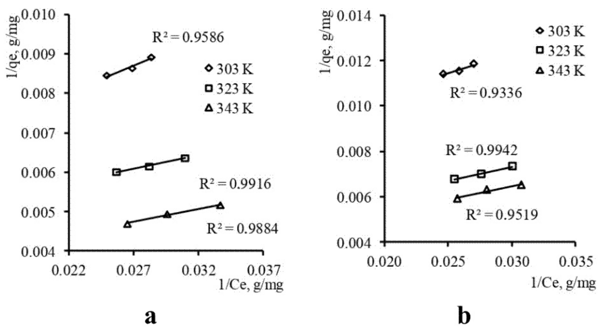


Fig. 2. Langmuir isotherms of oleic acid adsorption on AV-17-8 anion exchange resin: a – pre-dried adsorbent; b – air-dry adsorbent

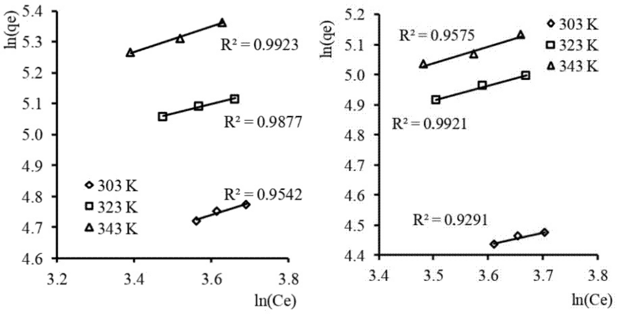
The Freundlich equation was used to determine the type of adsorption. The linear form of this equation is as follows:

$$\ln q_e=\ln k_F+\frac{1}{n}\ln C_e, \qquad (6)$$

where n and k_F are the adsorption isotherm constants.

The calculated values of the constant n (Fig. 3) at 303, 323 and 343 K are 1.83, 2.03, and 2.38 for adsorption on air-dry AV-17-8 anion exchange resin and 2.48, 3.29, and 2.48 for adsorption on pre-dried adsorbent, respectively. The obtained values of n are greater than 1. This indicates that the oleic acid adsorption on the anion exchange resin is physical.

The increase in the value of the K_F constant when the temperature was increased from 303 to 323 K indicates a significant increase in the adsorption capacity of the anion exchange resin. With a further increase in temperature to 343 K, the value of the K_F constant decreases slightly by about 5.5–10.0%.



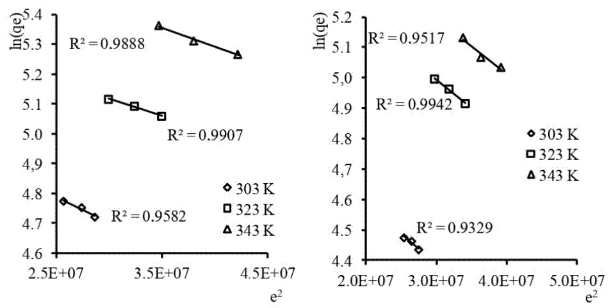
a **b**

Fig. 3. Freundlich isotherms of oleic acid adsorption on AV-17-8 anion exchange resin: a – pre-dried adsorbent; b – air-dry adsorbent

The Dubinin-Radushkevich adsorption model was used to calculate the activation energy of oleic acid adsorption on AV-17-8 anion exchange resin (Fig. 4). The linear form of the Dubinin-Radushkevich adsorption equation is as follows:

$$\ln q_e = \ln q_S - B\varepsilon^2, \tag{7}$$

where q_s is the theoretical isotherm adsorption capacity, mg/g; B is the adsorption isotherm constants, mol^2/kJ^2; and ε is the Polanyi potential.



a **b**

Fig. 4. Dubinin-Radushkevich isotherms of oleic acid adsorption on AV-17-8 anion exchange resin: a – pre-dried adsorbent; b – air-dry adsorbent

The Polanyi potential value was calculated using the equation:

$$\varepsilon = RT\ln\left(1+\frac{1}{C_e}\right), \tag{8}$$

where R is the universal gas constant, 8.314 J/(mol·K).

The mean energy of oleic acid adsorption on AV-17-8 anion exchange resin (Table 1) was calculated using of the adsorption isotherm constant B according to the equation:

$$E = (2B)^{-0.5}. \tag{9}$$

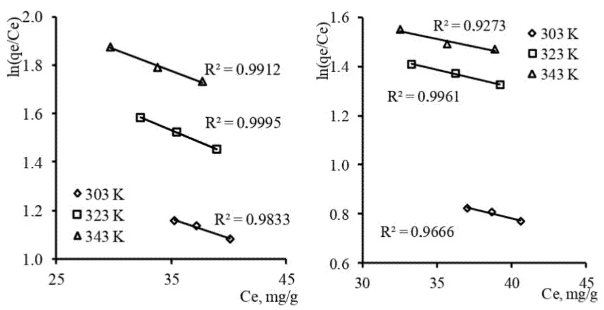
The mean energy of oleic acid adsorption on air-dry and pre-dried AV-17-8 anion exchange resin indicates that physical adsorption is observed on both adsorbents.

Table 1

The mean energy of oleic acid adsorption on AV-17-8 anion exchange resin

Temperature, K	The mean adsorption energy, kJ/mol	
	air-dry anion exchange resin	pre-dried anion exchange resin
303	5.2	7.8
323	5.2	6.6
343	5.3	6.2

The oleic acid adsorption equilibrium constant was determined to calculate the thermodynamic indicators of the acid adsorption. To this end, a plot $\ln(q_e/C_e)$ vs. C_e was used (Fig. 5).



a **b**

Fig. 5. The dependence of C_e versus $\ln(q_e/C_e)$ to determine the adsorption equilibrium constant: a – pre-dried adsorbent; b – air-dry adsorbent

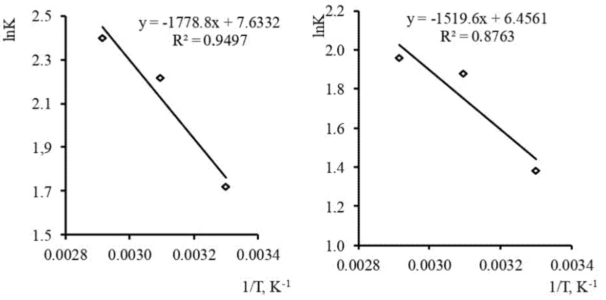
The oleic acid adsorption equilibrium constant *K* determined from Fig. 5 was used to calculate the following thermodynamic parameters of the oleic acid adsorption:

$$\Delta G = -RT\ln K, \tag{10}$$

$$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}, \tag{11}$$

where ΔG is the adsorption Gibbs free energy, kJ/mol; ΔS^0 is the adsorption entropy, kJ/(mol·K); and ΔH^0 is the adsorption enthalpy, kJ/mol.

A plot lnK vs. 1/T was used to determine the adsorption entropy and enthalpy (Fig. 6).



a b

Fig. 6. The dependence of 1/T versus lnK: a – pre-dried adsorbent: b – air-dry adsorbent

The thermodynamic parameters of the adsorption when air-dry and pre-dried anion exchange resin is used as the oleic acid adsorbent are shown in Table 2.

The negative values of the Gibbs free energy (Table 2) argue that oleic acid adsorption occurs spontaneously. The positive values of the activation entropy for oleic acid adsorption on air-dry and pre-dried anion exchange resin (53.7 J/(mol·K) and 63.5 J/(mol·K), respectively) confirm that conclusion. The thermodynamic indicators of oleic acid adsorption on AV-17-8 anion exchange resin correlate well with the data of carboxylic acids' adsorption on various types of adsorbents [11,12].

To recover acids from crude vegetable oils for subsequent transesterification, the adsorption of oleic acid from its solution in sunflower oil using an anion exchange resin with a content of 18.5 wt.% was investigated. It was found that at a temperature of 323 K, the adsorption degree of oleic acid reached 69.6%. The residual content of oleic acid in the vegetable oil was approximately 1 wt.%. At this acid concentration, the use of basic transesterification catalysts is feasible.

Conclusions

The research results of oleic acid adsorption on AV-17-8 anion exchange resin show that an increase in the adsorbent amount enhances the acid adsorption degree from the solution. The preliminary drying of the anion exchange resin reduces the completion time of the oleic acid equilibrium concentration in solution and increases the oleic acid degree adsorption. These results are obviously due to the high surface oleophobicity of air-dry anion exchange resin with high moisture content. Analysis of the experimental results using Langmuir, Freundlich and Dubinin-Radushkevich adsorption models shows that the oleic acid adsorption on AV-17-8 anion exchange resin is physical and spontaneous. In addition, this is confirmed by the mean adsorption energy of 5.2–7.8 kJ/mol (less than 8 kJ/mol), negative adsorption Gibbs free energy values, and positive value of the adsorption entropy.

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Table 2

Thermodynamic parameters of the oleic acid adsorption

Temperature, K	Adsorption equilibrium constant K	Gibbs free energy ΔG^0, kJ/mol	Enthalpy of adsorption ΔH^0, kJ/mol	Entropy of adsorption ΔS^0, J/(mol·K)
air-dry anion exchange resin AV-17-8				
303	4.0	–3.5	12.6	53.7
323	6.5	–5.0		
343	7.1	–5.6		
pre-dried anion exchange resin AV-17-8				
303	5.6	–4.3	14.8	63.5
323	9.2	–6.0		
343	11.0	–6.8		

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АДСОРБЦІЯ ОЛЕЇНОВОЇ КИСЛОТИ НА АНІОНІТІ АВ-17-8

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Досліджено адсорбцію олеїнової кислоти на аніонообмінній смолі АВ-17-8 із розчину в соняшниковій олії. Встановлено, що попереднє висушування аніонообмінної смоли прискорює досягнення рівноважної концентрації олеїнової кислоти в розчині та підвищує її ступінь адсорбції. Показано, що збільшення вмісту адсорбенту в розчині у всьому дослідженому інтервалі температур підвищує ступінь вилучення олеїнової кислоти з розчину. Встановлено, що з підвищенням температури адсорбції збільшується ступінь адсорбції олеїнової кислоти як повітряно-сухою аніонообмінною смолою, так і попередньо висушеним адсорбентом. Отримані результати проаналізовано із застосуванням моделей адсорбції Ленгмюра, Фрейндліха та Дубініна-Радушкевича. Показано, що адсорбцію олеїнової кислоти задовільно описує рівняння Ленгмюра. За розрахованими за моделлю Фрейндліха значеннями константи адсорбції встановлено, що адсорбція олеїнової кислоти на аніонообмінній смолі за умов досліджень є фізичною. Вказаний висновок підтверджують значення енергії активації адсорбції розраховані для моделі адсорбції Дубініна-Радушкевича. Визначено термодинамічні характеристики процесу адсорбції олеїнової кислоти на аніонообмінній смолі АВ-17-8. Отримані від'ємні значення вільної енергії Гіббса та додатні значення ентропії адсорбції свідчать, що адсорбція олеїнової кислоти на аніонообмінній смолі АВ-17-8 відбувається спонтанно.

Ключові слова: адсорбція, олеїнова кислота, соняшникова олія, аніонообмінна смола АВ-17-8, модель Ленгмюра, модель Фрейндліха, модель Дубініна-Радушкевича.

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