ISSN 2076-2429 (print)
ISSN 2223-3814 (online)

CHEMISTRY. PHARMACEUTICAL TECHNOLOGIES. BIOMEDICAL ENGINEERING

ХІМІЯ. ФАРМАЦЕВТИЧНІ ТЕХНОЛОГІЇ. БІОМЕДИЧНА ІНЖЕНЕРІЯ

UDC 544.7:543.5:543.64

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ADSORPTION OF QUINOLINE YELLOW FROM AQUEOUS SOLUTION BY SILICA GEL MODIFIED WITH CETYLPYRIDINIUM CHLORIDE

О.М. Жуковецька, О.М. Гузенко, І.Ю. Ігнатенко, К.В. Снігур, О.М. Чеботарьов, Д.В. Снігур. **Адсорбція хінолінового жовтого з водних розчинів силікагелем, модифікованим хлоридом цетилпіридинію**. В представленій роботі для ефективного концентрування аніонного харчового барвника хінолінового жовтого з розведених водних розчинів запропоновано адсорбент на основі силікагелю L 5/40, модифікованого цетилпіридиній хлоридом. Наявність катіонів цетилпіридинію на поверхні силікагелю було підтверджено методом інфрачервоної спектроскопії дифузного відбиття з Фур'є перетворенням. Досліджено та оптимізовано умови адсорбції хінолінового жовтого з розведених водних розчинів запропонованим адсорбентом. Показано, що використання модифікованого силікагелю дозволяє ефективно (>95 %) вилучати хіноліновий жовтий з водних розчинів. За оптимальних умов адсорбції (pH 2, наважка сорбенту 0,2 г, час сорбції 15 хв) визначено адсорбційну ємність модифікованого адсорбенту. Показано, що при підвищенні температури спостерігається зміна типу ізотерми з *L*-типу на *H*-тип. Показано, що ізотерми адсорбції добре описуються рівнянням Ленгмюра, а термодинамічні дослідження дозволяють говорити, що адсорбція має самочинний характер. Досліджено десорбцію хінолінового жовтого з поверхні силікагелю, модифікованого цетилпіридиній хлоридом. Відзначено, що при використанні розчинів сірчаної кислоти, гідроксиду натрію та дистильованої води десорбція не відбувається. Встановлено, що найефективнішим елюентом є 0,001 моль/л розчин додецилсульфату натрію в 0,1 моль/л гідроксиду амонію, а десорбція хінолінового жовтого відбувається за рахунок руйнування поверхневих іонних асоціатів аніонів барвника та закріплених на поверхні силікагелю катіонами цетилпіридинію. Отримані дані в подальшому можуть бути покладені в основу тест-системи для визначення хінолінового жовтого за відповідними кольориметричними шкалами або для твердофазної екстракції та сорбційно-спектроскопічного кількісного визначення хінолінового жовтого в деяких реальних зразках.

Ключові слова: хіноліновий жовтий, силікагель, хлорид цетилпіридинію, адсорбція, спектрофотометрія тягань

O. Zhukovetska, O Guzenko, I. Ignatenko, K. Snihur, O. Chebotarev, D. Snigur. **Adsorption of quinoline yellow from aqueous solution by silica gel modified with cetylpyridinium chloride.** In the current paper, adsorbent based on silica gel L 5/40 modified with cetylpyridinium chloride for the effective preconcentration of anionic food dye quinoline yellow from dilute aqueous solutions was proposed. The presence of cetylpyridinium cations on the silica gel surface was confirmed by the diffuse reflectance infrared fourier transform spectroscopy method. The adsorption conditions of quinoline yellow from dilute aqueous solutions with the proposed adsorbent were studied and optimized. It is shown that the use of modified silica gel allows efficient (>95 %) extraction of quinoline yellow from aqueous solutions. Under optimal sorption conditions (pH 2, sorbent dosage 0.2 g and sorption time is 15 min), the adsorption capacity of modified adsorbent was determined. It is shown that, with increasing temperature, a change in the isotherm type from the *L*-type to the *H*-type is observed. It was shown that adsorption isotherms were well described by the Langmuir equation. Thermodynamic studies have made it possible to

DOI: 10.15276/opu.2.64.2021.06

establish the spontaneous sorption.The desorption of qunoline yellow from the surface of silica gel modified with cetylpyridinium chloride was studied. It is shown that when using solutions of sulfuric acid, sodium hydroxide and distilled water, desorption does not occur. It was shown that the most effective eluent is a 0.001 mol/L solution of sodium dodecyl sulfate in 0.1 mol/L ammonium hydroxide, and desorption of quinoline yellow occurs due to the destruction of ion pairs of dye anions with cetylpyridinium cations fixed on the surface. The data obtained can then be used to develop a test system for determination of quinoline yellow via corresponding colorimetric scales or for quantitative solid phase extraction and adsorption-spectroscopic quantification of quinoline yellow in some real samples.

Keywords: quinoline yellow, silica, cetylpyridinium chloride, adsorption, spectrophotometry

Introduction

Food additives are widely used by food manufacturers, as they improve the taste, aroma, external attractiveness of goods [1]. Today, the production of most foods is almost impossible without the introduction of food colorants, especially synthetic dyes. Natural dyes are unstable and easily degraded, while synthetic ones give an intense color to food and are stable during storage. At the same time, the costs associated with their production are significantly lower compared to obtaining natural dyes. These advantages have encouraged manufacturers to use synthetic dyes. The most commonly used food dyes are tartrazine (E102), ponceau 4R (E124), sunset yellow FCF (E110), brilliant blue FCF (E133), patented blue V (E131), quinoline yellow (E104) and some others.

Analysis of literary data and problem statement

A large number of methods for the determination of food dyes have been proposed [1, 2]. A chromatographic, voltametric and spectrophotometric methods are commonly used in laboratory practice. Analysis of the current state of food dyes analytical chemistry are summarized in review articles [1, 2, 3]. It should be noted that in the vast majority, the determination of food dyes is preceded by the stage of their extraction or adsorption removal from the matrix or preconcentration [4, 5, 6]. In our opinion, among the preconcentration methods, adsorption occupies a special place due to its simplicity, high efficiency, and environmental friendly. In addition, it seems possible to combine adsorption preconcentration with some analytical techniques, such as diffuse refection spectroscopy, voltammetry etc [7...11].

The purpose and objectives of the study

In continuation of our previous studies on the investigation of acid-base properties of food dyes [12, 13], their adsorption preconcentration [14], as well as the development of methods for their voltammetric determination [15], the features of adsorption of quinoline yellow (QY) on silica gel (SG) modified with cetylpyridinium chloride (CPCl) are considered in the current work.

Materials and methods of research

The stock solution of QY with a concentration of $1 \cdot 10^{-2}$ mol/L, which was obtained by dissolving the exact weight of the dye in distilled water was used. Working solutions with lower concentrations were prepared by appropriate dilution of the stock solution immediately before use. To obtain a modified adsorbent silica gel L 5/40 and $1 \cdot 10^{-3}$ mol/L solution of CPCl were used. Electronic absorption spectra in the region of 380...780 nm were recorded on spectrophotometers Specord UV VIS and SF-56. The pH was measured on an I-160 potentiometer equipped with combined glass electrode ESKL-08M. Adsorption was studied in a static mode and mixing was performed with a automatic shaker AVU-1. Diffuse reflectance infrared Fourier-transform spectra (DRIFT-spectra) were obtained on an Perkin-Elmer Frontier FT-IR Spectrometer.

The modified sorbent (SG-CPCl) was obtained according to the method [14] for which 10 g of SG was weighed on analytical scales and placed into a conical flask. Then, 100 mL of $1 \cdot 10^{-3}$ mol/L CPCl solution was added into the flask, stopper and shaken for 60 minutes. The sorbent is then filtered off, washed with distilled water and dried. The presence of CPCl on the SG surface was confirmed by DRIFT. In the DRIFT spectra of SG-CPCl, absorption bands of siloxane bonds ≡Si-O-Si≡ at 1050 cm^{-1} and surface silanol groups bands at 3750 cm^{-1} are observed. Absorption bands were also recorded at 750 and 850 cm^{-1}, which correspond to the CH bonds bending vibrations in the pyridine ring and the band at 1600 cm^{-1} corresponded to the stretching vibration of the C=N bonds.

To study and optimize the conditions of QY adsorption via modified adsorbent SG-CPCl, on analytical scales weigh 0.1...0.4 g of adsorbent and place the samples in conical flasks. In a series of 50 mL volumetric flasks an aliquots of $1 \cdot 10^{-4}$ mol/L QY solution were intodused and diluted to the mark with a aqueous solutions with pH (1...7). The solutions are quantitatively transferred to conical flasks and shaken at various intervals (15...60 minutes).

ISSN 2076-2429 (print)
ISSN 2223-3814 (online)

The sorption recovery is calculated by the formula:

$$S = \frac{C_0 - C_e}{C_0} \cdot 100\% \ , \qquad (1)$$

where C_0 – initial concentration, mol/L; C_e – equilibrium concentration of the dye in the solution, mol/L.

Desorption of QY from the SG-CPCl surface was performed by 1...50 mL of solutions of hydrochloric, sulfuric, nitric and acetic acids (0.1...1.0 mol/L), sodium hydroxide and ammonium hydroxide (0.1...1.0 mol/L), as well as aqueous and ammonia solutions of sodium dodecyl sulfate (0.001...0.01 mol/L). The desorbate solution is filtered through a teflon filter and the concentration of QY was determined by spectrophotometric method. The desorption degree is calculated similarly to the sorption recovery.

Results and discussion

To optimize the conditions of adsorption of QY, the influence of the medium acidity, time and adsorbent dosage on the efficiency of dye removal were studied (Fig. 1).

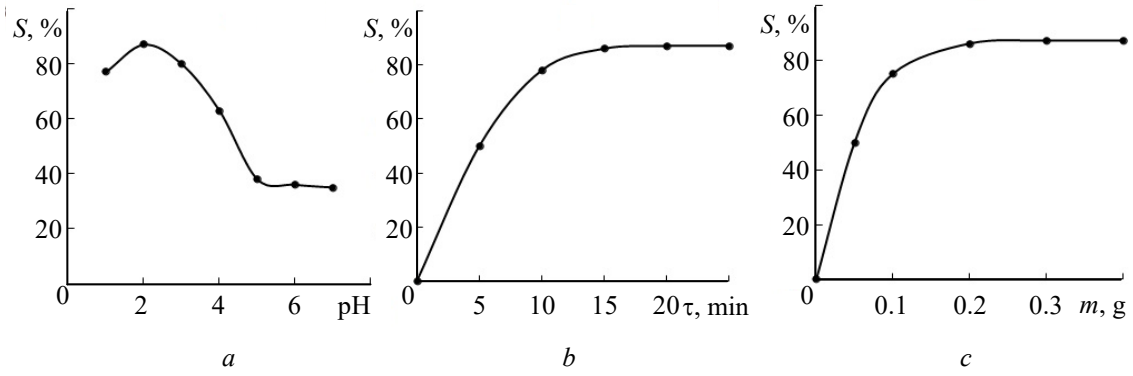

Fig. 1. Dependence of the QY sorption recovery by SG-CPCl on: pH (*a*); phase contact time (*b*); adsorbent dosage (*c*)

As can be seen from Fig.1 the quantitative adsorption of QY is achieved by carrying out adsorption in static mode with 0.2 g of SG-CPCl adsorbent at pH 2 for 15 minutes.

For the study of QY adsorption mechanism onto SG-CPCl, the adsorption isotherms at 293K and 317K were obtained (Fig. 2).

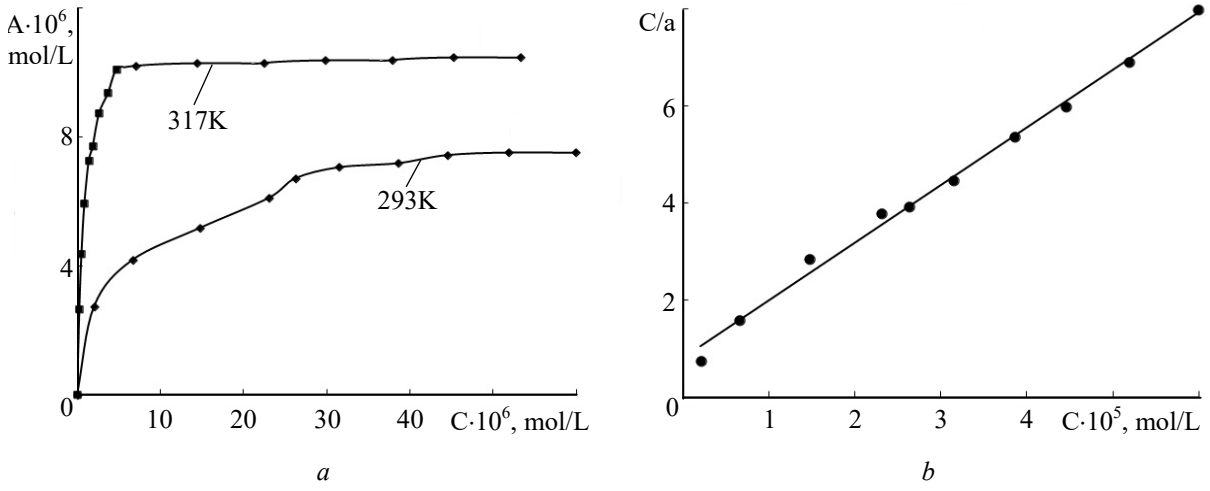

Fig. 2. Adsorption isotherms of QY on SG-CPCl at different temperatures (*a*) and adsorption isotherm at 293 K linearized in the coordinates of the Langmuir equation (*b*)

As can be seen from Fig. 2*a*, the obtained isotherms can be attributed to L-type (Fig. 2, curve 1) and H-type (Fig. 2, curve 2) according to the Giles classification [16]. The Langmuir and Freundlich equations are used satisfactorily to describe L- and H-type isotherms. It was found that in the case of adsorption of azo dyes (carmoisine, tartrazine, sunset yellow FCF) by the sorbent SG-CPCl [14] and, in this case, the best adsorption isotherms are described by the Langmuir equation. For example, the adsorption isotherm at 293K, which is linearized in the coordinates of the Langmuir equation, is shown in Fig. 2b.

Based on the obtained adsorption isotherms and their linearized forms, the maximum adsorption capacity (A_∞) of QY on the SG-CPCl, the constant of adsorption equilibrium (K) and corresponding thermodynamic parameters are calculated and summarized in the Table 1.

Table 1

Adsorption and thermodynamic characteristics of the studied system

Dye	A_∞, μmol/g		$K \cdot 10^{-5}$		ΔG^0, kJ/mol		ΔH^0, kJ/mol	ΔS^0, J/mol·K	
	293 K	317 K	293 K	317 K	293 K	317 K		293 K	317 K
Quinoline Yellow	8.4	11.5	1.2	1.6	–29.2	–31.0	–7.5	74.2	77.2

As can be seen from Table, the standard Gibbs energy takes on negative values that indicate the spontaneous nature of the adsorption process. The positive values of ΔH^0 indicate the exothermic adsorption process. An increase in the value of K and A_∞ with temperature increase testifies the predominantly chemical interactions accompanying the adsorption of QY by SG-CPCl surface.

The desorption of QY from the SG-CPCl surface was investigated. As desorbents used solutions of acids (hydrochloric, sulfuric, nitric, acetic, salicylic, succinic, oxalic, citric, caprylic), bases (sodium hydroxide, ammonium hydroxide) varying the concentration and volume of the desorbent. The organic solvents (ethanol, propanol, acetone, acetonitrile, tetrahydrofuran) and anionic and nonionic surfactants solutions (sodium dodecyl sulfate, sodium tetradecyl sulfate, sodium hexadecyl sulfate, triton X-100) were also tested as desorbents. In general, it should be noted that solutions of acids do not elute the QY from the SG-CPCl surface. It should be noted that bases and organic solvents have a low elution capacity, and the desorption degree not exceed 60 %. Anionic surfactants solutions elute the QY much better, which may be additional evidence of predominantly chemical interactions between the SG-CPCl surface and the QY. Solutions of sodium dodecyl sulfate proved to be the most effective eluents, and the desorption degree increases with increasing pH, which is due to the transition of the dye into highly charged anionic forms and destruction of the surface ionic pairs. In turn, quantitative desorption is achieved in an alkaline medium (pH~11) by elution of the QY with 5 mLof 0.001 mol/L solution of sodium dodecyl sulfate in 0.1 mol/L ammonium hydroxide.

Conclusions

Thus, as a result of this study, the process of quinoline yellow food dye adsorption onto silica gel modified with cetylpyridinium chloride was investigated. It was found that adsorption is mainly chemical in nature, and the quantitative removal of the dye is achieved at pH 2 within 15 minutes. The main thermodynamic and adsorption parametres were determined. It is shown that quantitative desorption occurs only under conditions of destruction of surface ionic pairs, and the most effective eluent is a 0.001 mol/L solution of sodium dodecyl sulfate in 0.1 mol/L ammonium hydroxide.

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Received October 08, 2021
Accepted December 06, 2021