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Adsorption of di-2-pyridyl ketone salicyloylhydrazone on silica gel: characteristics and isotherms

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Abstract

The adsorption of DPKSH onto silica gel was investigated, at $25 \pm 1\,^{\circ}$C and pH 1, 4.7 and 12. For the same DPKSH concentration interval, the minimum required time of contact for adsorption maximum at pH 4.7 was smaller than at pH 1 and the maximum amount of DPKSH adsorbed per gram of silica at pH 1 is smaller than at pH 4.7. At pH 12 the DPKSH adsorption onto silica gel was not significant. The adsorption data followed Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherms. The maximum amount of solute adsorbed ($m_{\mathrm{ads}}^{\mathrm{max}}$) and the adsorption constant, K_L, were derived from Langmuir isotherm. The Freundlich constants $1/n$ and K_F related, respectively, to the energetic heterogeneity of adsorption sites and an empirical constant were evaluated. The mean sorption free energy (E) of DPKSH adsorption onto silica gel was calculated from D–R isotherm indicating a physical adsorption mode. Finally, conductimetric titrations showed the silica particle basicity and acidity as 0.002 and 0.3 mmol g^{-1}, respectively.

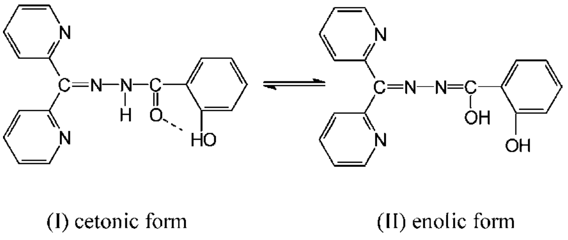
Keywords: Adsorption; DPKSH; Silica gel; Isotherms

1. Introduction

A variety of nitrogen containing heterocyclic hydrazones have drawn much attention because of its analytical potentialities. These compounds have been widely used as analytical reagents because they give sensitive reactions with most of metal ions forming coloured chelates [1–9]. In these chelates the aroylhydrazones can behave as bidentate, tridentate or tetradentate ligands when they have donor atoms in appropriate positions [10–12].

A typical aroylhydrazone described by the C=N–N group used in the present work is di-2-pyridyl ketone salicyloylhydrazone (DPKSH) which was formerly synthesised by Garcia-Vargas et al. [10].

In aqueous/ethanolic solutions, DPKSH presents a tautomeric equilibrium (Eq. (1)). Structures I and II represent, respectively, the form cetonic and enolic:



(1)

In acid solutions, DPKSH exhibits an equilibrium between the neutral (RN) and the protonated ($\mathrm{RNH^+}$) forms (Eq. (2)). The equilibrium is related with the dissociation constant of DPKSH, represented by K_1.

Considering the protonation of a pyridine nitrogen atom, the extension of this equilibrium is given by the respective ionisation constant, $\mathrm{p}K_1 = 3.5$, at aqueous solution containing 3% ethanol (v/v) [10]:

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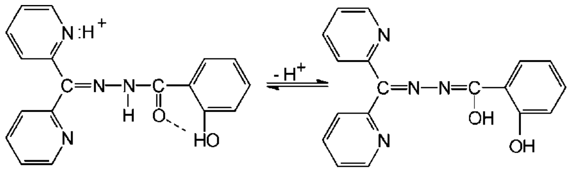
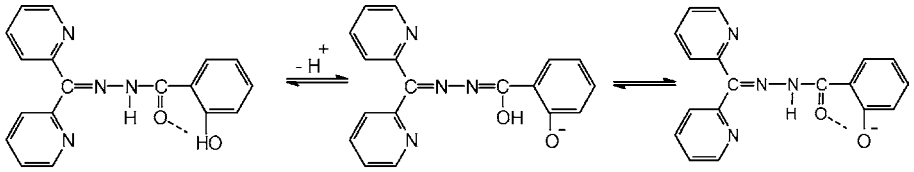


$$R(NH)^{+} \rightleftharpoons RN + H^{+} \qquad K_1 \tag{2}$$

A second protonation equilibrium must be considered from the DPKSH's tautomeric balance, involving the enolic form and resulting in ionic species (Eq. (3)):



$$R(OH) \rightleftharpoons RO^{-} + H^{+} \qquad K_2 \tag{3}$$

Equilibrium (Eq. (3)) is quantitatively represented by the respective ionisation constant, being $pK_2 = 6.85$, at aqueous solution containing, as in the present work, 3% ethanol (v/v) [10].

DPKSH solutions present a visible adsorption onto glass when stored in glass bottles. This characteristic of the DPKSH and its wide use as chelator for many metals led to this study about the adsorption of DPKSH onto silica, in different pH conditions.

The organofunctionalised silica gel, which has many advantages [13,14] in respect to other supports [15–18], has been largely studied with regard to the preconcentration capacity. Its selective capacity for transition metal ions in respect to alkaline ions is useful for analysis of samples as seawater and natural water. However, many silica support cannot be used in any condition of pH neither for different strips of concentration.

Silica gel is an amorphous inorganic polymer with siloxane groups (Si–O–Si) and silanol groups (Si–OH) [19–22]. The most of siloxane groups are in the internal part of silica and few of them can be found on the surface. The most of silanol groups are on the surface and some of them can be found in the internal region.

Silanol groups are responsible for the physical and chemical modifications that occur on the silica surface. Silica is usually considered as an acid oxide, however, in the concept of acid–base theory, surface oxygen and oxygen of hydroxyl may be considered as basic sites and these surface basic sites may play an important role in surface processes such as adsorption. Bunker et al. [23] pointed out that lone pair electrons on bridged oxygen and silanol groups can function as a Lewis base and Brønsted base, respectively.

2. Experimental

2.1. Reagents and solutions

All reagents and solvents were of analytical-reagent grade. The synthesis of DPKSH was performed as previously reported by Garcia-Vargas et al. [10]. The ligand was obtained from the reaction of stoichiometric amounts of di-2-pyridyl ketone and salicyloylhydrazide in ethanol. Few drops of concentrated hydrochloric acid were added and the mixture was refluxed for 60 min. After cooling, distilled water was added to a 1:3 volume ratio (ethanol:water). Several drops of sodium hydroxide solution were added to the refluxed solution to increase the pH to approximately 5. The product was collected on a Büchner funnel and recrystallised twice from an ethanol–water solution. After synthesis, the melting point of the product was verified to be $173 \pm 1\,^{\circ}C$ and it is in excellent agreement with the literature [10]. Stock $10^{-3}\,mol\,L^{-1}$ DPKSH solutions were prepared by dissolving the reagent in ethanol 100%.

The pH of the solutions were adjusted at 1 with HCl solution; at pH 4.7 with a buffer solution as sodium acetate and glacial acetic acid $0.1/0.1\,mol\,L^{-1}$ and, pH 12 with NaOH solution.

Aldrich Chemical silica gel, 60 (230–400 mesh) Grade 9385 was used. Initially the silica gel was washed by contact with HCl solution ($0.1\,mol\,L^{-1}$), in a bath during 24 h, to remove any impurity and adsorbed metal ions, then it was collected on a Büchner funnel with a filter paper and repeatedly washed with deionised water until the filtrate is almost neutral (pH ≈ 6). Then the washed silica was dried in a dessecator during 4 days to remove adsorbed water.

Copper solution was prepared dissolving $Cu(NO_3)_2$ in $3\,mol\,L^{-1}$ NH_4OH aqueous solution and the respective concentration was determined by electrogravimetric method.

The cuvetes, all glass and plastic vessels were washed with 10% HNO_3 solution followed by distilled and deionised water.

The stock DPKSH solution was stored in plastic vessels to avoid the adsorption on glass surfaces.

2.2. Apparatus

The UV-Vis spectra were registered on a HITACHI U3000 spectrophotometer using 1.00 cm quartz cells. The pH measurements were performed with a Metrohm 654 pH meter equipped with a Metrohm glass electrode of which the Ag/AgCl reference was filled with $3\,mol\,L^{-1}$ NaCl. Centrifugation of the mixtures was carried out with an Incibrás—Spin IV centrifuge. The agitation of the mixtures was performed on a shaker TE-140 Tecnal with controlled velocity. The room temperature was kept constant at 25 ± 1 °C, in all of the experiments.

Conductance measurements were made on a Micronal B330 conductance meter with cell Analyser 7A04 with a constant K of $1.0\,cm^{-1}$. The titrations were carried out using HCl (10^{-2}, 10^{-3} and $10^{-4}\,mol\,L^{-1}$) and NaOH (10^{-2}, 10^{-3} and $10^{-4}\,mol\,L^{-1}$) solutions. The temperature was maintained at 25.0 ± 0.1 °C with a thermostatic Heto-Lab equipment. The suspensions containing silica gel were stirred using a PTFE-coated magnetic stirrer.

2.3. Adsorption experiments

DPKSH adsorption kinetics and isotherms were determined using the solution depletion method. In stoppered plastic tubes 0.2 g the silica gel was shaken for specific periods with an aqueous solution (10 mL) of DPKSH containing 3% ethanol (v/v).

The supernatants were separated by centrifuging the mixtures and the concentration of DPKSH was determined using the absorption measurement at 343 nm ($pH = 1$), 319 nm ($pH = 4.7$) and 304 nm ($pH = 12$). The sorbed concentration of DPKSH at equilibrium was calculated by the difference in the absorbance of the aliquots drawn before and after shaking. The blank was prepared in the same way but without DPKSH. The temperature was kept constant at 25 ± 1 °C and a constant shaking speed was kept in the shaking table.

The number of silanol groups present in the silica gel was determined in the same way as the DPKSH adsorption. Then, about 100 mg of the dry silica was added to a 10 ml of a $0.1\,mol\,L^{-1}$ copper solution. The suspension was then automatically shaken for 1 h and, the silica was separated by centrifugation for 3 min. Supernatant aliquots were subjected to complexometric titration using the appropriate buffer and indicator solutions and a standard solution of EDTA. The quantity (mol) of Cu^{2+} adsorbed per unit mass of silica can be calculated using the following equation [24]:

$$N_{Cu} = \frac{N_0 - N_{eq}}{m} \tag{4}$$

where m is the mass of silica and N_{Cu}, N_0 and N_{eq} are, respectively, the number of moles of copper attached per gram of silica, the initial number of moles of copper and the copper (mol) present in the solution at equilibrium with the solid phase.

3. Results and discussion

3.1. Spectral characteristics of DPKSH

DPKSH spectra were registered in the UV-Vis region for solutions with different pH (1, 4.7 and 12) at 3% ethanol/water (v/v). Fig. 1 shows the spectra of DPKSH and quite different behaviours are observed as a function of pH. The analytical wavelengths were established from these spectra and the following values were considered to each pH condition: 343 and 319 nm, respectively, for pH 1 and 4.7. The study of DPKSH adsorption in pH 12 was not followed because the preliminary experiments did not show significant adsorption on silica gel and the change in the constitution of silica was visible, probably due to its partial dissolution in the basic medium.

The analytical curves for DPKSH aqueous solutions containing 3% ethanol (v/v) were obtained with pH adjusted at 1 and 4.7. The respective parameters calculated using the least square method are:

$$\text{pH 1}: \quad A_{343\,nm} = 2.09 \times 10^4 C_{DPKSH} - 0.016, \quad r^2 = 0.9999 \tag{5}$$

$$\text{pH 4.7}: \quad A_{319\,nm} = 1.98 \times 10^4 C_{DPKSH} + 0.029, \quad r^2 = 0.9996 \tag{6}$$

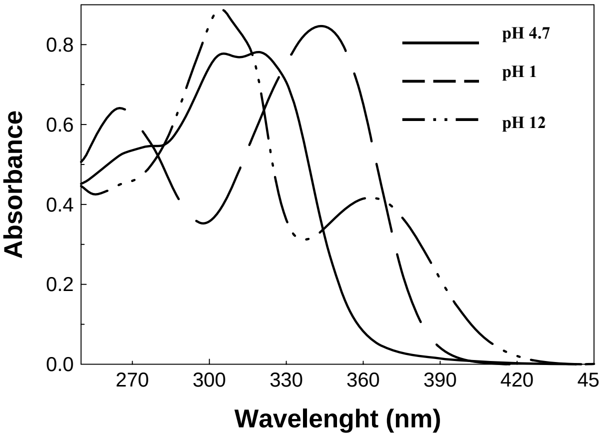


Fig. 1. Absorption spectra of DPKSH aqueous solutions containing 3% (v/v) ethanol, at pH 1, 4.7 and 12 ($DPKSH = 4.05 \times 10^{-5}\,mol\,L^{-1}$).

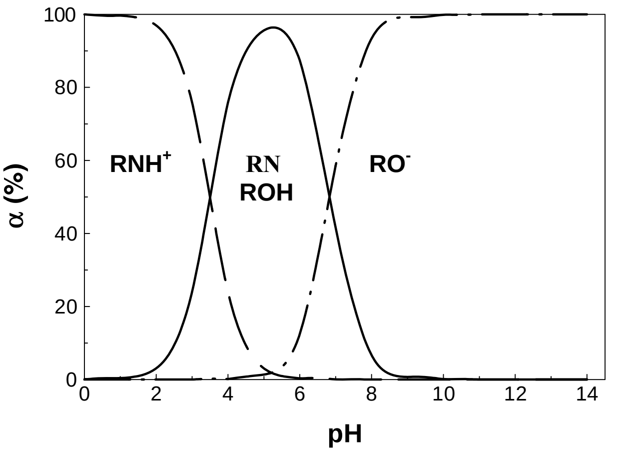


Fig. 2. Distribution diagram for the species of DPKSH in aqueous solution containing 3% (v/v) ethanol ($T = 25 \pm 1\,^{\circ}\mathrm{C}$, $K_1 = 3.16 \times 10^{-4}$ and $K_2 = 1.41 \times 10^{-7}$).

With the ionisation constants ($K_1 = 3.16 \times 10^{-4}$ and $K_2 = 1.41 \times 10^{-7}$) of DPKSH the distribution diagram can be constructed as shown in Fig. 2. It shows that different species (RNH^+, RN and RO^-) predominate in different ranges of pH and, at pH 1, 4.7 and 12 used in the present adsorption studies, one has almost total predominance of, respectively, RNH^+, RN and RO^-. Then, it is possible to consider that from the analytical curves, the molar absorptivities of RN^+ and RN species are, respectively, $(2.09 \pm 0.01) \times 10^4$ and $(1.98 \pm 0.02) \times 10^4\,\mathrm{mol\,L^{-1}\,cm^{-1}}$.

3.2. Silica adsorption sites (silanol groups) and basicity/acidity of silica

The number of silanol groups available in the silica was determined as the number of copper, N_{Cu}. This number was found to be 12.3 mg ($0.19\,\mathrm{mmol\,g^{-1}}$) and it corresponds to approximately $0.39\,\mathrm{mmol\,OH^-\,g^{-1}}$ considering a ratio of 2:1 for silanol groups coordinated by each copper ion.

The basicity/acidity of silica was determined following the conductance of silica unmodified and modified with DPKSH at pH 1 and 4.7, in aqueous solutions of ethanol 3%, during titrations with HCl and NaOH. The behaviour of the solvents water and ethanol was here considered because they are polar and amphiprotic (amphoteric) molecules, i.e. they are proton acceptor and proton donor. The respective dissociation equilibrium (autoprotolysis) of water and ethanol (EtOH) are:

$$2H_2O \rightleftharpoons H_3O^+_{(SOLV)} + \mathbf{OH}^-_{(SOLV)} \tag{7}$$

$$2EtOH \rightleftharpoons \mathbf{EtO}^-_{(SOLV)} + EtOH^+_{2(SOLV)} \tag{8}$$

Considering both of the equilibria, the aqueous solutions containing ethanol 3% may be considered as having a total positive charge $[P^+] = [H_3O^+] + [EtOH_2{}^+]$ and a total negative charge $[N^-] = [OH^-] + [EtO^-]$. The very low percentage of ethanol used in this study leads to consider as predominant the auto-ionisation of water. The quantity of those ionic species are very low but they were detected in the conductance titrations with very diluted NaOH and HCl solutions ($10^{-4}\,\mathrm{mol\,L^{-1}}$). A simple solution of ethanol–water has a very low conductance. However, the conductance varies significantly when a solution of HCl or NaOH is added. Two linear segments were observed in the profile curve relative to the titration of 5.00 ml of ethanol 3%. The intersection between these segments corresponds to a consumption of 1.2×10^{-7} mol of H^+ from HCl probably due to the protonation of OH^- and EtO^-. The titration with NaOH solution showed a consumption of 1.7×10^{-7} mol of OH^-, probably by the H_3O^+ and $EtOH_2{}^+$ ions. Higher concentrations of HCl or NaOH solutions used in the titrations did not show any consumption by the ionic species from water or ethanol.

Titrations of aqueous/ethanol 3% solution of DPKSH $1.0 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$ with HCl and NaOH $10^{-4}\,\mathrm{mol\,L^{-1}}$ showed consumption of 1.5×10^{-7} mol of H^+ and 2×10^{-7} mol of OH^-, respectively, showing a behaviour quite similar to water/ethanol 3%. Titration with HCl $1.0 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$ showed a consumption of 9.0×10^{-7} mol and this value may be attributed to the protonation of OH^-, EtO^- and DPKSH (5.0×10^{-7} mol).

Silica in water/ethanol 3% was also titrated with HCl and NaOH in three different concentrations. With HCl $1.0 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$ a consumption of 2.4×10^{-7} mol was detected corresponding to the intersection of two linear segments found in the conductance titration curve. The difference between this value and 1.2×10^{-7} mol of H^+ from titration of water/ethanol 3% may be attributed to the protonation of the basic groups of silica gel, surface siloxane groups (Si–O–Si and $Si–O^-$). The basicity of the silica was found to be $0.002\,\mathrm{mmol\,g^{-1}}$. Higher HCl concentrations showed only one linear segment of conductance variation as a function of titrant volume.

Titration of silica with NaOH $1.0 \times 10^{-2}\,\mathrm{mol\,L^{-1}}$ showed a consumption of 2.9×10^{-5} mol of OH^- in the reaction with the silanol groups (Si–OH). Considering the silica weighing in the range 0.105 ± 0.005 g the number of silanol groups (acidity) is $0.3\,\mathrm{mmol\,g^{-1}}$ showing a very good concordance with the number found with the number of copper.

Titrations of silica modified with DPKSH did not show any difference with the results obtained for silica free of DPKSH adsorption. This is probably due to the very low mass of DPKSH adsorbed in 0.1 g of silica, weigh used for the titrations.

3.3. Kinetics of adsorption

A series of batch experiments was conducted to assess the minimum time necessary to obtain a maximum adsorption of DPKSH onto silica. These experiments were carried out at pH 1 and 4.7, chosen on the basis of the DPKSH equilibria characterised by the presence of predominantly RNH^+ and RN species which correspond to, respectively, the protonated and the neutral DPKSH as shown in Fig. 2.

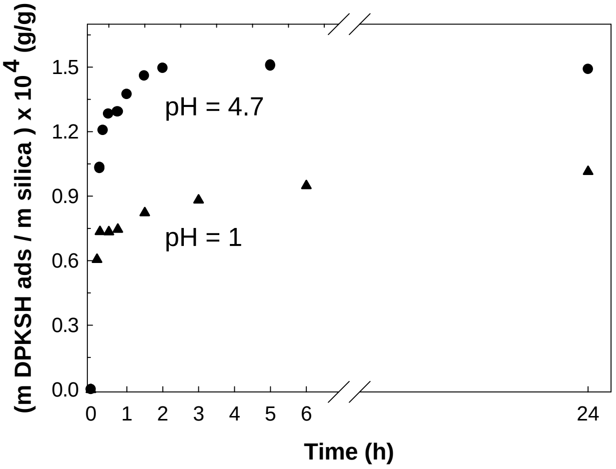


Fig. 3. Dependence of adsorbed mass of DPKSH per unit mass of silica gel on time of contact at pH 1 and 4.7.

The sorption of 4×10^{-5} mol L^{-1} DPKSH aqueous solution containing 3% ethanol (v/v) on silica gel was studied at pH 1 and 4.7. The variation of the mass of DPKSH adsorbed per gram of silica as a function of time is shown in Fig. 3, for both of the pH. The maximum sorption (minimum absorbance) is achieved after 5 h for pH 4.7 and 6 h for pH 1 and a higher adsorption is observed at pH 4.7 than at pH 1.

3.4. Adsorption isotherms

For thermodynamic consideration in terms of adsorption isotherms, many experimental values were obtained for the adsorption of DPKSH on silica gel and plotted. To describe the adsorption equilibria three commonly used mathematical expressions were tested with these experimental data. These equations correspond to the Freundlich, Langmuir and Dubinin–Radushkevich (D–R) isotherm models [25–28].

The Langmuir model [26] was originally developed to represent chemisorption on a set of well-defined localised adsorption sites having same adsorption energy, independent of the surface coverage and with no interaction between adsorbed molecules. Maximum adsorption is noticed when surface of adsorbent is covered with a monolayer of adsorbate. The Langmuir adsorption isotherm based on the kinetic consideration is given by

$$m_{\text{ads}} = \frac{m_{\text{ads}}^{\text{max}} K_{\text{L}} C_{\text{eq}}}{1 + K_{\text{L}} C_{\text{eq}}} \qquad (9)$$

where m_{ads} represents the amount of DPKSH adsorbed per unit weight of silica (g/g silica), $m_{\text{ads}}^{\text{max}}$ the amount of solute adsorbed (g) per gram of silica required for monolayer coverage of the surface, also called monolayer capacity, C_{eq} the concentration of DPKSH in solution at equilibrium conditions (g l^{-1}) and K_{L} is the constant of Langmuir related to the equilibrium constant of adsorption process.

Fig. 4 shows the experimental data m_{ads} versus C_{eq} for pH 1 (a) and pH 4.7 (b). The fit of these curves was realised using the software Jandel Sigma Plot 3.0 by adjusting the experimental data to Eq. (9). The use of this software permits the fit of the curve and it was not necessary to linearise the equation. However, the results were confirmed when both kind of calculations were done. The parameters K_{L} are 5.3 ± 1.5 and 144 ± 25 L g^{-1} and $m_{\text{ads}}^{\text{max}}$ are (1.5 ± 0.4) and (0.27 ± 0.02) mg (DPKSH) g^{-1} (silica) for pH 1 and 4.7, respectively. The solid lines represented in the curves, Fig. 4(a) and (b), were calculated using the parameters obtained with the experimental values and an excellent fit is observed. The effect of pH on the adsorption of DPKSH to silica was marked by a higher adsorption at the higher pH, in the same region of DPKSH equilibrium concentration. This may be attributed to the fact that the surface of silica and the DPKSH are positively charged at lower pH, and the electrostatic interactions between the DPKSH and the silica surface are not favourable. Adsorption at pH 4.7 appears more favourable probably because the DPKSH are

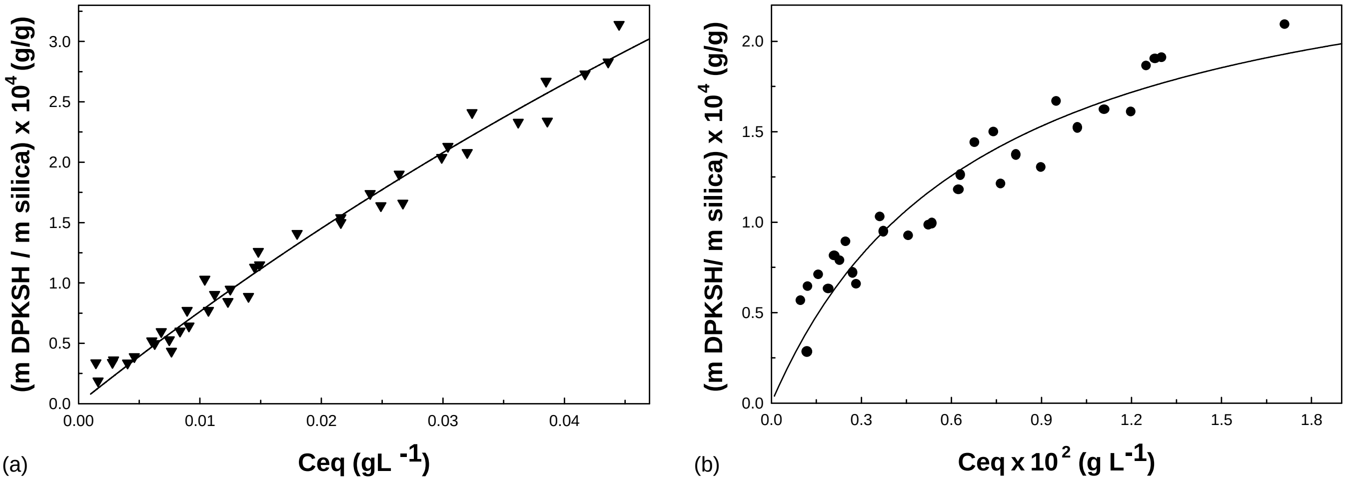


Fig. 4. Adsorption isotherms of DPKSH onto silica gel at pH 1 (a) and pH 4.7 (b) ($T = 25 \pm 1$ °C). Solid lines correspond to the Langmuir model fitting.

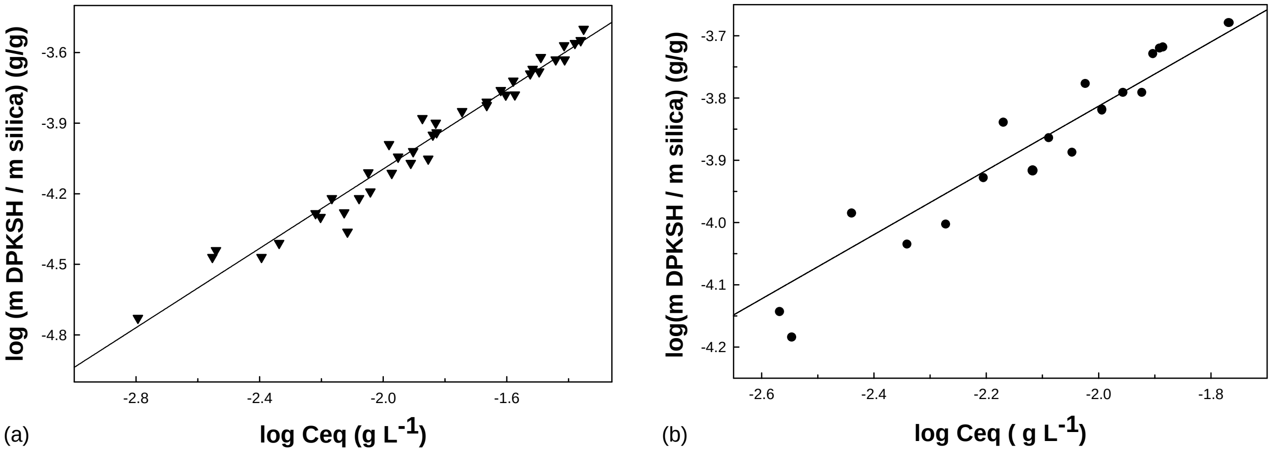


Fig. 5. Adsorption isotherms of DPKSH onto silica gel at pH 1 (a) and pH 4.7 (b) ($T = 25 \pm 1\,^{\circ}$C). Solid lines correspond to the Freundlich model fitting.

predominantly in the neutral form as can be seen in the distribution diagram for the species of DPKSH (Fig. 2).

The Freundlich adsorption isotherm [25], one of the most widely used mathematical description, usually fits the experimental data over a wide range of concentration. This isotherm gives an empirical expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies.

The Freundlich equation is of the form:

$$m_{\mathrm{ads}} = K_{\mathrm{F}} C_{\mathrm{eq}}^{1/n} \qquad (10a)$$

where m_{ads} and C_{eq} have the same definitions as previously presented for the Langmuir isotherm, K_{F} the empirical constant and $1/n$ is related to the energetic heterogeneity of adsorption sites. The logarithmisation of Eq. (10a) gives the following linear equation:

$$\log m_{\mathrm{ads}} = \log K_{\mathrm{F}} + \frac{1}{n}\log C_{\mathrm{eq}} \qquad (10b)$$

The plots of $\log m_{\mathrm{ads}}$ versus $\log C_{\mathrm{eq}}$ are shown in Fig. 5 at pH 1 (a) and pH 4.7 (b). The Freundlich constants $1/n$ and K_{F} were determined from the slope and the intercept of the plots. The numerical value of adsorption capacity K_{F} and n indicating the energy and intensity are, respectively, $3.9 \pm 0.9\,\mathrm{mg\,g^{-1}}$ and 1.2 ± 0.2 for pH 1 and, $1.7 \pm 0.5\,\mathrm{mg\,g^{-1}}$ and 1.9 ± 0.1 for pH 4.7. Freundlich adsorption isotherm does not predict any saturation of the solid adsorbent surface, thus infinite surface coverage is predicted mathematically. The values of $1/n$ obtained for the adsorption of DPKSH in both pH were less than 1 (0.83 at pH 1 and 0.59 at pH 4.7), indicating favoured adsorption. The lower value of $1/n$, obtained for pH 4.7, is indicative of stronger adsorption affinity for DPKSH at this pH than at pH 1. The solid lines represented in the curves, Fig. 5(a) and (b), were calculated using the parameters obtained with the experimental values and an excellent fit is observed.

To distinguish between physical and chemical adsorption, the data were applied to D–R isotherm model [27]. The adsorption is postulated within an adsorption "space" close to adsorbent surface. This model features the heterogeneity of energies over the surface. The linear form of D–R isotherm is

$$\ln C_{\mathrm{ads}} = \ln K_{\mathrm{DR}} - B\varepsilon^2 \qquad (11)$$

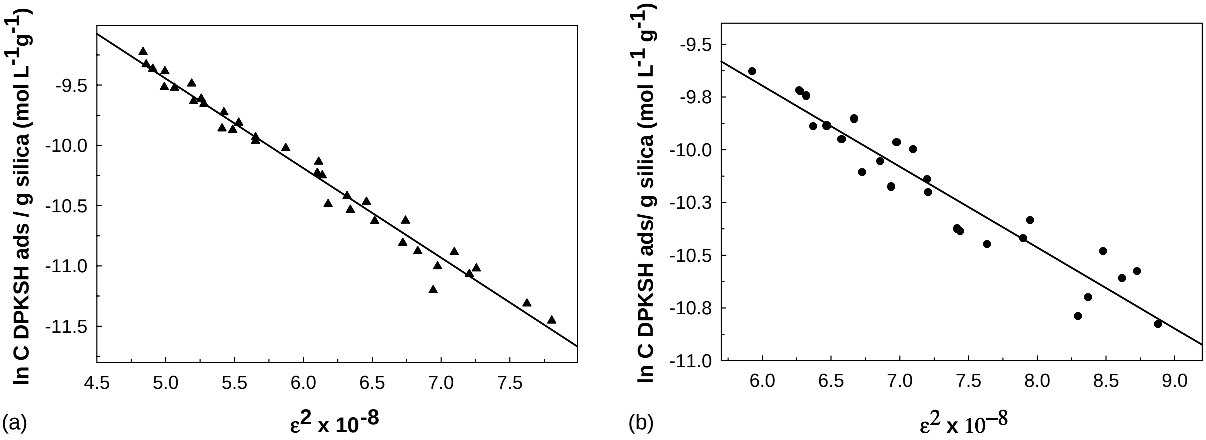


Fig. 6. Adsorption isotherms of DPKSH onto silica gel at pH 1 (a) and pH 4.7 (b) ($T = 25 \pm 1\,^{\circ}$C). Solid lines correspond to the Dubinin–Radushkevich model fitting.

where C_{ads} is the amount of DPKSH adsorbed per unit mass of the silica ($\mathrm{mol\,g^{-1}}$), K_{DR} the maximum amount of DPKSH adsorbed, B is a constant with dimensions of energy and Polanyi potential $\varepsilon = RT\ln[1 + (1/C_{\mathrm{eq}})]$, where R is a gas constant in $\mathrm{kJ\,K^{-1}\,mol^{-1}}$ and T is the temperature in K.

Fig. 6(a) and (b) shows the linear relationship between $\ln C_{\mathrm{ads}}$ and ε^2, for both of the pH values 1 and 4.7. The linear regression method was applied and the values of B and K_{DR} were obtained as the slope and the intercept of the curves (a) and (b) giving $(-7.4 \pm 0.2) \times 10^{-9}\,\mathrm{J^2\,mol^{-2}}$ and $(3.25 \pm 0.02) \times 10^{-3}\,\mathrm{mol\,g^{-1}}$ for pH 1 and $(-3.8 \pm 0.2) \times 10^{-9}\,\mathrm{J^2\,mol^{-2}}$ and $(6.2 \pm 0.1) \times 10^{-4}\,\mathrm{mol\,g^{-1}}$ for pH 4.7.

According to Saeed et al. [29] if the surface is considered heterogeneous and an approximation to a Langmuir isotherm is chosen as a local isotherm for all sites that are energetically equivalent then the quantity $B^{1/2}$ can be related to the average sorption energy (E) as

$$E = \frac{1}{\sqrt{-2\mathrm{B}}} \tag{12}$$

which is the mean free energy of the transfer of 1 mol of solute from infinity to the surface of silica gel. The numerical values of E calculated from the Eq. (12) are 8.2 and $11.5\,\mathrm{kJ\,mol^{-1}}$ for pH 1 and 4.7, respectively.

4. Conclusions

The adsorption of DPKSH onto silica gel follows Langmuir, Freundlich and D–R adsorption models at both of the pH studied. The maximum amount of DPKSH (g) per gram of silica obtained from Eq. (9), Langmuir isotherm, at pH 1 is higher than at pH 4.7.

The adsorption is more intensive at pH 4.7 than at pH 1 and the values of K_{L} confirm this behaviour, because K_{L} is higher ($144\,\mathrm{L\,g^{-1}}$) at pH 4.7 than at pH 1 ($5.3\,\mathrm{L\,g^{-1}}$).

In the range of DPKSH concentration 1.8×10^{-2} until $4.8 \times 10^{-2}\,\mathrm{g\,L^{-1}}$, it was only possible to work at pH 1. The restriction of the solubility of DPKSH is smaller at pH 1, and we managed to work on a band of larger concentration because DPKSH is predominantly in the protonated form ($\mathrm{RNH^+}$). That justifies the difference in the maximum amount of DPKSH (g) per gram of silica adsorbed at pH 1 and 4.7.

The constants obtained from the three isotherms related to the ratio between grams of DPKSH and volume (L) or mass of silica (g), i.e. K_{L}, K_{F} and K_{DR} show the same relationship as the maximum amount of DPKSH adsorbed onto silica gel at the same interval of concentration (from 0 to $1.9 \times 10^{-2}\,\mathrm{g\,L^{-1}}$) because their values are higher at pH 4.7 than at pH 1.

Parameters n evaluated from Freundlich isotherm are 1.2 (pH 1) and 1.9 (pH 4.7), i.e. higher than 1. These values characterise the presence of energetically heterogeneous adsorption sites and this heterogeneity is higher at pH 4.7 than at pH 1, probably because the distribution of $\mathrm{OH^-}$ and $\mathrm{SiO^-}$ groups are different and at pH 1 the most of the sites are protonated.

The mean free energy, E, characterises a physical adsorption at both of the pH studied and the predominance of van der Waals forces.

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