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Treatment of wastewaters containing acid, reactive and direct dyes using aminosilane functionalized silica

Abstract: Aminosilane modified silica was prepared and investigated for the adsorption of textile dyes such as C.I. Acid Orange 7 (AO7), C.I. Reactive Black 5 (RB5) and C.I. Direct Blue 71 (DB71) from aqueous media and wastewaters. The values of the sorption capacities obtained from the Langmuir isotherm model were: 5.3 mg g\(^{-1}\), 58.7 mg g\(^{-1}\) and 72.2 mg g\(^{-1}\) for AO7, DB71 and RB5, respectively. The affinity series of the dyes for the modified silica can be presented as follows: C.I. Reactive Black 5 > C.I. Direct Blue 71 > C.I. Acid Orange 7. The influence of anionic surfactant (SDS) and sodium chloride on dye sorption was investigated in a system containing 100 mg L\(^{-1}\) dye and 0.1-1 g L\(^{-1}\) SDS or 1-25 g L\(^{-1}\) NaCl. The sorption capacities decrease with increasing concentration of SDS in the solution. Retention of AO7 and RB5 was reduced in the presence of NaCl. A satisfactory agreement of the experimental data with the pseudo second-order kinetic model was found. Effectiveness of the aminosilane modified silica in raw textile wastewater purification was confirmed.

Keywords: dye sorption, modified silica, wastewater purification, kinetic studies, dyes removal

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1 Introduction

Industrial wastewaters are one of the most hazardous pollutants of natural waters. Textile wastewaters belong to industrial wastewaters containing low levels of biodegradable and chemically stable compounds. Chemical treatment of textiles requires the use of numerous chemicals (dyes, salts, acids, bases, surfactants, organic and inorganic auxiliaries) as well as enormous amounts of water [1]. The amount of water used for chemical treatment of textiles ranges from several to a few hundred liters for 1 kg of textiles depending on the kind of product and process as well as equipment. The least water absorbing dying processes are based on direct and acid dyes in which the water consumption is 10-40 L kg\(^{-1}\). In the case of reactive dyes, water consumption is 100-215 L kg\(^{-1}\) depending on the type of jigger [2]. In textile three-shift (24 h per a day and night) plants equipped with 40 dyeing machines, assuming an average periodical dyeing capacity of 2000-5200 m\(^{3}\) per 24 h and 7-10 baths during one dyeing process, an enormous amount of wastewater (2400-5200 m\(^{3}\)) is produced per 24 h [1,3]. Therefore it is desirable to minimize this amount by purifying at least a part of the waste stream and making an attempt to re-use the purified water in production. In textile wastewater purification, biological, chemical and physical methods and combinations thereof are applied. A system of biological and chemical purification with relatively few stages can reduce impurities significantly. Sewage purification by means of filtration, coagulation, active sedimentary deposit in the nitrification-denitrification system, membrane separation and ozonation allows for 86% COD (Chemical Oxygen Demand) reduction, 52% nitrogen reduction, 50% total carbon reduction and 90% total organic carbon reduction [1].

Table 1 presents the parameters characterizing wastewaters after each of the partial purification stages in a textile plant equipped with a complex sewage-treatment plant designed based on BAT (Best Available Techniques)
guidelines for the textile industry [1]. Introduction of adsorption process to this multi-approach purification of wastewaters can be another attractive treatment process if the adsorbent is inexpensive and readily available [4,5]. Many studies have recently focused on the development of alternative sorbents produced from renewable and low-cost materials to replace activated carbons and traditional ion exchangers. Some of these materials exhibit relatively high sorption capacities [5]. One of the low-cost sorbents is silica. As follows from literature data, the yield of adsorption of dyes on different types of silica is mainly attributed to surface modification using aminosilane compounds [6-11]. Functionalized silica of this type is characterized by higher sorption capacities for organic dyes compared with unmodified ones [8-10]. Particularly good sorption results were obtained by Jesionowski et al [8,9] for the sorption of C.I. Direct Red 81, C.I. Acid Green 16, C. I. Acid Violet 1, C.I. Acid Red 18 and C.I. Reactive Blue 19 on silica modified by means of N-2-(aminoethyl)-3-aminopropyltrimethoxysilane. The applicability of amino-modified magnetic silica in removal of C.I Acid Orange 10 and C.I. Acid Orange 12 was confirmed by Atia et al. [7].

In this study, the immobilization of (3-aminopropyl) triethoxysilane on silica was performed in order to obtain a low cost sorbent selective for the removal of the three textile dyes C.I. Acid Orange 7, C.I. Reactive Black 5, and C.I. Direct Blue 71 from aqueous solutions containing different auxiliaries and from wastewaters. Kinetic and equilibrium parameters of adsorption were calculated.

2 Experimental procedure

2.1 Materials

Three different dyes commonly used in the textile industry were purchased from Sigma-Aldrich (Germany) and used without further purification. Their characteristics are listed in Table 2. Precipitated Syloid® 244 silica (W.R. Grace Davision, US) modified with (3-aminopropyl) triethoxysilane (Sigma-Aldrich, Germany) was applied as a sorbent. The other chemicals were obtained from POCh (Poland) and were of analytical grade.

2.2 Procedure of silica surface modification

The silica surface was modified with (3-aminopropyl) triethoxysilane. An appropriate amount of the silane was hydrolysed in a system of methanol: water (4:1, v/v) and then applied on the silica surface by the method described in detail in [12,13]. A simplified mechanism for the modification process is presented in Scheme 1.

The elemental contents of the sorbent were measured using a Vario El Cube instrument (Elementar Analysensysteme GmbH, Germany), and found to be as follows: 1.44% C, 1.48% O, 0.61% N.

In order to characterise the parameters of the porous structure of silica, specific surface area and pore volume were determined using an Accelerated Surface Area and Porosimetry 2020 instrument (Micromeritics Instrument Co., USA). The BET specific surface area of the modified silica powders was determined to be 257 m² g⁻¹, and the volume of the pores of the material was found to be 0.16 cm³ g⁻¹.

The presence of desired functional groups was confirmed by Fourier transform infrared spectra (FT–IR), recorded on an EQUINOX 55 spectrophotometer (Bruker, Germany). Fig. 1 presents the FT–IR spectrum of unmodified and modified silica Syloid®244. The spectrum of SiO₂ reveals the presence of Si–O–Si (vₛ: 1096 cm⁻¹, vₐₙ: 805 cm⁻¹), Si–OH (vₛ: 960 cm⁻¹) and Si–O (δ: 470 cm⁻¹) characteristic bonds, where vₛ and vₐₙ stand for the symmetric and asymmetric stretching vibrations, while δ represents

Table 1: Parameters of raw textile wastewaters and after successive purification stages [1].

| Parameters        | Raw textile wastewaters | Filtration/coagulation | Biological treatment | Membrane filtration | Ozonation |
|-------------------|-------------------------|------------------------|----------------------|---------------------|-----------|
| pH (at 25°C)      | 9.56                    | 8.15                   | 8.20                 | 8.42                | 8.33      |
| Conductivity (at 25°C (mS cm⁻¹)) | 3.03                   | 3.0                    | 2.75                 | 2.64                | 2.58      |
| COD (mgO₂ dm⁻³)   | 895.00                  | 1095.00                | 250.00               | 139.00              | 129.00    |
| Total N (mgN dm⁻³) | 9.12                   | 18.57                  | 8.56                 | 4.53                | 4.3       |
| Total C (mgC dm⁻³) | 348.3                   | 387.3                  | 213.4                | 179.5               | 173.6     |
| TOC (mg dm⁻³)     | 256.3                   | 324.3                  | 50.61                | 27.86               | 24.21     |

COD-chemical oxygen demand, TOC-total organic carbon
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bending vibrations. The other bands, namely the O–H stretching vibration (3600-3200 cm⁻¹) and the low-intensity band at ~1630 cm⁻¹, are assigned to water physically bound in silica. In the spectrum of silica modified with aminosilane, the intensity of the O–H band increases slightly compared to that recorded for unmodified silica. This increase could be a result of overlapping of the stretching vibrations of N–H groups from the modifier used. The appearance of a low-intensity band at 1650-1560 cm⁻¹, assigned to the bending vibration of N–H, confirms the success of the surface modification with aminosilane. In the range 2965-2850 cm⁻¹, there is a band assigned to the stretching vibrations of the C–H bond. The intensity of this band increased in comparison with that recorded for unmodified silica.

| Dyes characteristic | C.I. Acid Orange 7 | C.I. Reactive Black 5 | C.I. Direct Blue 71 |
|---------------------|------------------|---------------------|--------------------|
| Name                | sodium salt of 4-(2-hydroxynaphthylazo) benzenesulfonic acid | tetrabismaleate salt of 4-amino-5-hydroxy-3,6-bis(4-(2-sulfoxy)ethyl)sulfonyl)phenylazo)-2,7-naphthalenedisulfonic acid | tetrabismaleate salt of 3-[[E]-[E]-[E]-[E]-2-(6-amino-1-oxo-3-sulfonatonaphthalen-1-yl)diazene]-6-sulfonatonaphthalen-1-yl)diazene]naphthalene-1,5-disulfonate |
| UPAC name and 3D molecular structure | | | |
| Empirical Formula | C₁₆H₁₁N₂NaO₄S | C₂₆H₂₁N₅Na₄O₁₉S₆ | C₄₀H₂₇N₇Na₄O₁₃S₄ |
| Molecular weight (g mol⁻¹) | 350.32 | 991.82 | 1029.88 |
| Colour Index Number | 15510 | 20505 | 34140 |
| Producer | Sigma-Aldrich, Germany | | |

Scheme 1: Simplified diagram of silica modification with (3-aminopropyl)triethoxysilane.

Figure 1: FT-IR spectra of unmodified and modified silicas.
2.3 Adsorption kinetics of acid, reactive and direct dyes

Batch experiments were made to investigate the effect of contact time and to determine kinetic parameters. The adsorption kinetics of dyes onto the aminosilane functionalized silica was carried out at five different initial concentrations (50, 100, 200, 300 and 500 mg L\(^{-1}\)) by adding 50 mL of dye solution to 0.5 g of adsorbent. The suspensions were stirred continuously (180 rpm) at 25°C. After different time intervals (0-60 min) the samples were filtered under vacuum and analyzed using a UV-vis spectrophotometer Specord M-42 (Carl Zeiss, Germany) at the maximum absorbance wavelengths (484 nm, 587 nm and 598 nm for AO7, RB5 and DB71, respectively). The dye concentration in the aminosilane functionalized silica phase at specific times \(q_t\) as well as the colour removal efficiency \(\%R\) were calculated as:

\[
q_t = \left(\frac{C_0 - C_t}{w}\right) \times V
\]

\[
R(\%) = \left(\frac{C_0 - C_t}{C_0}\right) \times 100
\]

where \(C_0\) and \(C_t\) are the concentrations of the dye in the solution before and after sorption, respectively (mg L\(^{-1}\)), \(V\) is the volume of the solution (L) and \(w\) is the weight of the sorbent (g).

Decolourization of real textile wastewaters (denoted as samples I, II and III) obtained from a textile company containing different reactive dyes and auxiliaries was also studied using the batch method. In this experiment, a dosage of 0.5 g of aminosilane-functionalized silica was shaken with 50 mL of real wastewater for 1 to 60 min. During this experiment, small samples were withdrawn at various times in order to estimate the removal of dyes by the analysis of absorbance values at the maximum absorbance wavelength. Prior to recording of the spectra, wastewater samples I and II were diluted by a factor of 10 after specific phase contact time intervals, whereas the other samples were not diluted.

2.4 Isotherms

Adsorption isotherms were obtained by placing the samples of 0.5 g of dry modified silica in a series of flasks containing 50 mL of dye solution at the desired initial concentrations (50-3000 mg L\(^{-1}\)) at room temperature. The flasks were conditioned for 1 h at 180 rpm. Later on, the residual concentration of dye was estimated.

2.5 Effect of the addition of auxiliaries on dye uptake

The influence of sodium chloride and SDS (sodium dodecyl sulphate) anionic surfactant on dye sorption on aminosilane-functionalized silica was studied by agitating the solution containing 100 mg L\(^{-1}\) of dye and between 1 to 25 g L\(^{-1}\) of NaCl, or 0.1 to 1 g L\(^{-1}\) of SDS. Dyes concentration after 60 min of phase contact time was measured spectrophotometrically at the maximum absorbance wavelengths.

3 Results and discussion

3.1 Kinetic studies of adsorption of acid, reactive and direct dyes on aminosilane modified silica

The kinetic adsorption of C.I. Acid Orange 7, C.I. Reactive Black 5, and C.I. Direct Blue 71 on aminosilane-modified silica was measured for various initial dye concentrations (50-500 mg L\(^{-1}\)) at room temperature. The dependences of the amounts of dye adsorbed on the aminosilane-modified silica, \(q_t\) vs. \(t\) are shown in Fig. 2.

As can be seen, for the given concentrations, the amount of dye adsorbed increased rapidly within the first 5 minutes of sorption. A phase contact time of 10 min was sufficient to attain the state of equilibrium and the complete removal of C.I. Direct Blue 71 from the solutions with initial concentrations of 50 and 100 mg L\(^{-1}\). For the dye solutions with initial concentrations of 200, 300 and 500 mg L\(^{-1}\), the equilibrium state of sorption for this dye was attained after 30 min. Liu et al. [14] also observed that the rate of adsorption of methyl orange dye on quaternary ammonium polyethyleneimine modified silica was very fast initially and tapered off as equilibrium was approached. This result is very encouraging because the equilibrium time is an important parameter for wastewater treatment. The amounts of C.I. Direct Blue 71 adsorbed at equilibrium using the aminosilane modified silica were 5.0, 10.0, 20.0, 23.1 and 25 mg g\(^{-1}\) for the dye solutions with initial concentrations of 50, 100, 200, 300 and 500 mg L\(^{-1}\), respectively. Calculated values of the colour removal efficiency \(\%R\) decreased from 99.9% to 51.3% with the increase of the initial dye concentration from 50 to 500 mg L\(^{-1}\), respectively. Similar dependences were obtained for the adsorption kinetics of C.I. Reactive Black 5 and C.I. Acid Orange 7 on the aminosilane modified silica. The values of the colour removal efficiency calculated...
Figure 2: Kinetic curves of C.I. Acid Orange 7 (a), C.I. Reactive Black 5 (b) and C.I. Direct Blue 71 (c) sorption on the aminosilane modified silica (conditions: initial dyes concentrations: 50-500 mg L\(^{-1}\), volume: 50 mL, sorbent mass: 0.5 g, agitation speed: 180 rpm, temperature: 25°C).
at the equilibrium state (after 20 min) decreased from 99.9% \((q_e = 5.0 \, \text{mg g}^{-1})\) to 40% \((q_e = 19.9 \, \text{mg g}^{-1})\) for C.I. Reactive Black 5 and from 80% \((q_e = 4.0 \, \text{mg g}^{-1})\) to 39% \((q_e = 19.5 \, \text{mg g}^{-1})\) for C.I. Acid Orange 7 with the increase of the initial dye concentration from 50 to 500 mg L\(^{-1}\). Mahmoodi et al. \cite{15} also reported that adsorption of acidic dyes by the aminosilane modified silica was very intense and reached equilibrium very quickly at low initial concentration. It was concluded that at a fixed adsorbent dosage, the amount of adsorbed dyes increased with the increasing concentration of solution, but the percentage of adsorption decreased. In other words, the residual dye concentration will be higher for higher initial dye concentrations. In the case of lower concentrations, the ratio of initial number of dyes moles to the available adsorption sites is low and subsequently, the fractional adsorption becomes independent of initial concentration \cite{15}.

Various kinetic models such as pseudo first-order (PFO), pseudo second-order (PSO), modified pseudo first-order (MPFO), pseudo-n-order (PnO), intraparticle diffusion model (IDM), mixed 1,2-order equation (MOE) and fractal-like MOE adsorption kinetics have been used to describe the kinetics of adsorption at the solid/solution interface \cite{16}. However, the most popular and well-known classical kinetic equations in the adsorption process are the pseudo first-order and pseudo second-order:

\[
\log(q_e - q_t) = \log(q_e) - \frac{k_1 q_e}{2.303} t
\]

(3)

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t
\]

(4)

where: \(q_t\) and \(q_e\) (mg g\(^{-1}\)) are the amounts of the dye sorbed at time \(t\) and at equilibrium, \(k_1\) (min\(^{-1}\)) is the rate constant of the pseudo-first order sorption, and \(k_2\) (g mg\(^{-1}\) min\(^{-1}\)) is the pseudo-second order rate constant \cite{16-18}.

When sorption proceeds by diffusion through a boundary, the kinetics most likely follow the pseudo first-order Lagergren equation. The modelling of the effect of initial dye concentrations using this equation, by plotting \(\log(q_e - q_t)\) versus time allows for the calculation of the rate constant \(k_1\) and the equilibrium sorption capacity \(q_e\). It was observed that there is a deviation from the straight line during the first 15 min of sorption for all initial concentrations, signifying that pseudo-first order kinetics are not applicable for the systems in question. Table 3 shows the pseudo first-order rate constants, \(k_1\) and \(q_e\), as well as the determination coefficients \(R^2\). The values of the equilibrium capacity determined from this model and the experimental ones were very different from each other. The determination coefficients were very low, in the range 0.402-0.915 for C.I. Acid Orange 7, 0.157-0.947 for C.I. Reactive Black 5 and 0.812-0.908 for C.I. Direct Blue 71. This suggests that sorption of the dyes by the aminosilane modified silica is not diffusion-controlled and the process does not follow the pseudo first-order sorption expression of Lagergren.

To investigate the possibility of dyes being transported within pores of the aminosilane modified silica, the experimental data were fitted with the Weber and Morris intraparticle diffusion plot of the amount of dye sorbed per unit mass of sorbent against the square root of contact time according to the equation:

\[
q_t = k_i t^{0.5} + C_i
\]

(5)

where: \(k_i\) (mg g\(^{-1}\) min\(^{0.5}\)) is the intraparticle diffusion rate, and \(C_i\) is the intercept.

The values of \(k_i\) obtained from the plots of \(q_t\) vs \(t^{0.5}\) for the acid, reactive and direct dyes at five different initial concentrations were linear but did not pass through the origin. The intercepts of the plots reflect the boundary layer effect. The larger the intercept, the greater the contribution of the surface sorption in the rate limiting step. The \(C_i\) values increased from 3.77 to 18.38 for C.I. Acid Orange 7, from 4.98 to 16.83 for C.I. Reactive Black 5 and from 4.99 to 19.64 for C.I. Direct Blue 71 with the increasing initial dye concentration in the system. External mass transfer of dye anions to the sorbent particles in this case is significant, especially during the initial reaction period. The determination coefficients, \(R^2\), listed in Table 3, were rather low, in the range 0.300-0.844, 0.299-0.953 and 0.799-0.886 for C.I. Acid Orange 7, C.I. Reactive Black 5 and C.I. Direct Blue 71, respectively, which contradicts the applicability of this model.

Kinetic data were further treated with the pseudo-second order kinetic model. Table 3 shows a decrease of the values of the rate constants, \(k_2\), with increasing initial dye concentration. The values of \(q_e\) determined from the plot of \(t/q_t\) vs \(t\) not only for C.I. Acid Orange 7 but also for C.I. Reactive Black 5 and C.I. Direct Blue 71 were fitted to be very close to the experimental values of equilibrium sorption capacities, \(d_{eq}\), indicating the pseudo second-order model sufficiently described the sorption of the dyes on the aminosilane modified silica for the range of initial concentrations used. For example, the values of \(q_e\) calculated from this model for C.I. Reactive Black 5 were 4.99, 9.97, 13.07, 15.5 and 19.9 mg g\(^{-1}\) (\(R^2 \geq 0.999\)), and the corresponding experimental values were found to be 5.0, 10.0, 13.0, 15.3, 19.9 mg g\(^{-1}\). The determination coefficients that reflect the conformity between the model and experimental values were all higher than 0.999. A satisfactory agreement of the experimental data with the pseudo second-order
The kinetic model was observed by Atia et al. [7] for sorption of C.I. Acid Orange 10 on the modified magnetic silica with immobilized 3-aminopropyltriethoxysilane. According to Ofomaja [19], when the pseudo second-order kinetics is applicable, the rate limiting step is chemical sorption or chemisorption involving valence forces through sharing or exchange electrons between the sorbent and sorbate as covalent forces. This means that the sorption of acid, reactive and direct dyes on the aminosilane modified silica may be due to chemical reaction between the positive charge on the modified silica and the negative charge on the dye anions.

### 3.1.1 Effect of phase contact time on wastewaters purification

Effectiveness of the aminosilane modified silica in raw textile wastewater purification was confirmed in the batch experiments. The effluents from the textile industry containing different reactive dyes and auxiliaries (Table 4) were conditioned with the sorbent for 1 to 60 min. The UV-Vis spectra of the wastewaters before and after sorption were recorded as presented in Fig. 3. Significant colour reduction was observed after 1 min of phase contact time for sample III. The increase of phase contact time to 60 min enhanced the purification yield of sample III, where and 88.5% reduction of colour was observed. The absorbance value at the maximum wavelength after 60 min was reduced from 0.8767 to 0.1008. The aminosilane modified silica was ineffective in purification of samples I and II: the values of absorbance at the maximum wavelengths were reduced only about 27.2% and 17.3%, respectively, after 60 min of phase contact time.

### 3.2 Isotherm studies

The analysis of equilibrium data for the adsorption of C.I. Acid Orange 7, C.I. Direct Blue 71 and C.I. Reactive Black 5 onto the aminosilane modified silica has been carried out using the linear forms of the Langmuir [20] and Freundlich [21] equations. In relation to the adsorption systems involving the extractions of large organic compounds like dyes from aqueous solutions, the Langmuir and Freundlich isotherm expressions are the most commonly used [22]. According to Allen et al. [22] the relative size of the sorbate molecule and the molecular sieving effect of the sorbent have been shown to affect the equilibrium system.

The linear forms of the Langmuir and Freundlich equations are:

\[
C_e = \frac{1}{q_o b} + \frac{C_e}{Q_o} \tag{6}
\]

\[
\log q_e = \log k_f + \frac{1}{n} \log C_e \tag{7}
\]

where: \( Q_o \) (mg g\(^{-1}\)) is the Langmuir monolayer sorption capacity, \( b \) (L mg\(^{-1}\)) is the Langmuir adsorption constant, \( k_f \) (mg g\(^{-1}\)) is the Freundlich adsorption capacity, and \( 1/n \) is the
Table 4: Photo images of the wastewaters samples before and after sorption on the aminosilane modified silica.

| Dye bath composition                                                                 | Samples of wastewaters before and after decolourization on the aminosilane modified silica |
|--------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------|
| Sample I: Reactive Blue 21 - 3.348% (2309 mg L⁻¹), Bezaktiv Blau SFR - 0.0434% (30 mg L⁻¹), Na₂CO₃, Na₂SO₄, Perigen LDR (liquid dispersing and sequestering agent); pH=11.38 |
| Sample II: Reactive Yellow 145 - 0.5% (694.4 mg L⁻¹), Reactive Red 195 - 0.97% (1347.2 mg L⁻¹), Reactive Blue 221 - 0.05% (69.5 mg L⁻¹) NaCl, NaOH, Na₂CO₃, Perigen LDR; pH=11.1 |
| Sample III: Reactive Black 5 - 7.5% (6250 mg L⁻¹), Na₂CO₃, NaOH, NaCl, Perigen LDR; wastewater after ozonation pH=6.64 |

Figure 3. Absorbance spectra of acid raw wastewaters purified by means of the aminosilane modified silica (conditions: wastewaters composition (see Table 3): (a) sample I, (b) sample II, (c) sample III, volume: 50 mL, sorbent mass: 0.5 g, agitation speed: 180 rpm, temperature: 25°C, phase contact time: 1-60 min).
Freundlich constant related to the surface heterogeneity. The above-mentioned Langmuir and Freundlich constants were evaluated from the intercept and the slope of the linear plots of $c/q_e$ vs. $c$ ($Q_e$ and $b$) and $\log q_e$ vs. $\log c_e$ ($k_F$ and $1/n$), respectively. The Langmuir model denotes the monolayer adsorption and is applicable to homogeneous adsorption, where the adsorption of each adsorbate molecule onto the surface has equal adsorption activation energy. Unlike the Langmuir equation, the Freundlich expression is an empirical equation based on adsorption on a heterogeneous surface, and is not restricted to monolayers. It is known that the Freundlich model is generally applicable for low concentrations.

The adsorption isotherm parameters were calculated and are listed in Table 5. The correlation coefficient parameters demonstrate that the Langmuir model is acceptable ($R^2 > 0.9$). The obtained values of the sorption capacities ($Q_e$) are 5.3 mg g$^{-1}$ ($R^2=0.999$), 58.7 mg g$^{-1}$ ($R^2=0.978$) and 72.2 mg g$^{-1}$ ($R^2=0.924$) for C.I. Acid Orange 7, C.I. Direct Blue 71 and C.I. Reactive Black 5, respectively. Taking these values into consideration, the affinity series of the dyes for the aminosilane modified silica can be presented as follows: C.I. Reactive Black 5 > C.I. Direct Blue 71 > C.I. Acid Orange 7. The molecular size, number of sulfonic groups in the dye as well as their arrangements in the space are probably the crucial factors that determine adsorption capacity values. The Langmuir constant $b$ reflects the affinity of sorbent for the sorbate. The highest value of $b$ equal to 0.616 was determined for the C.I. Acid Orange 7 dye and implied strong bonding of the dye to this sorbent. For the C.I. Reactive Black 5 and C.I. Direct Blue 71 dyes, the $b$ values were found to be 0.0015 and 0.0042, respectively. To determine if the adsorption process is favourable or unfavourable for the Langmuir type sorption process, the dimensionless constant $R_L$ was calculated [23]. A value of $R_L > 1$ indicates unfavourable sorption, $R_L = 1$ linear sorption, $0 < R_L < 1$ favourable sorption and $R_L = 0$ irreversible sorption. The $R_L$ values for the C.I. Acid Orange 7, C.I. Reactive Black 5 and C.I. Direct Blue 71 dyes on the aminosilane modified silica were equal to 0.008, 0.1818 and 0.0869, respectively. This confirmed that the aminosilane modified silica is favorable for the adsorption of the above mentioned dyes under the experimental conditions. The results obtained are in agreement with the observation by Atia et al. [7] concerning C.I. Acid Orange 10 (AO10) removal from aqueous solutions on silica modified by means of 3-aminopropyltriethoxysilane in the presence and the absence of magnetite particles (Fe$_3$O$_4$). The monoamine modified magnetic silica (MAMMS) displayed higher and faster adsorption relative to the magnetite free case (MAMPS) for the AO10 dye. The maximum adsorption capacities of MAMPS and MAMMS towards AO10 were found to be 48.98 mg g$^{-1}$ and 61.33 mg g$^{-1}$, respectively. Adsorption of the dye on both MAMMS and MAMPS fit the Langmuir model. Lower values of the adsorption capacities compared with C.I. Acid Orange 7 dye using silica gel modified with 3-aminopropyltriethoxysilane were found for C.I. Acid Orange 12 in the studies carried out by Donia et al. [24]. The adsorption capacities increased with temperature rise from 11.8 mg g$^{-1}$ to 15.5 mg g$^{-1}$ [24]. Mahmoodi et al. [15] studied the interactions between three acidic dyes such as C.I. Acid Red 14 (AR14), C.I. Acid Black 1 (ABI) and C.I. Acid Blue 25 (AB25) and silica and found that the monolayer adsorption capacities did not exceed 0.180 mg g$^{-1}$. But the maximum dye adsorption capacities of the amine functionalized silica nanoparticle for AR14, ABI and AB25 were 434 mg g$^{-1}$, 250 mg g$^{-1}$ and 167 mg g$^{-1}$, respectively [13]. A brief list of the maximum sorption capacities of the modified silica sorbents for various dyes, including the results obtained in this work, is presented in Table 6 [14,15,24-29].

The Freundlich model provided a better fit than that of the Langmuir model for the C.I. Reactive Black 5 and C.I. Direct Blue 71 sorption on the amionosilane modified silica (Fig. 4). The correlation coefficients were found to be 0.988 for C.I. Reactive Black 5 and 0.987 for C.I. Direct Blue 71. The magnitude of $k_F$ and $n$ values of the Freundlich model showed easy uptake of the reactive and direct dyes with a high adsorption capacity of adsorbent. Large value of $k_F$ means higher adsorption capacity. The $k_F$ values, listed in Table 5, reveal easy uptake of the reactive and direct dyes by the modified silica. The favorable adsorption of C.I. Reactive Black 5 and C.I. Direct Blue 71 confirmed by low values of $1/n$ lower, over the concentration range used, indicating strong interactions between the dye anions and the aminosilane modified silica.

### Table 5: Langmuir and Freundlich isotherm parameters for the sorption of acid, reactive and direct dyes on the aminosilane modified silica.

| Dye                     | Freundlich model | Langmuir model |
|-------------------------|------------------|----------------|
|                         | $n$              | $k_F \text{ (mg g}^{-1}\text{)}$ | $R^2$ | $b \text{ (L mg}^{-1}\text{)}$ | $Q_e \text{ (mg g}^{-1}\text{)}$ | $R^2$ |
| C.I. Acid Orange 7      | 3.360            | 1.459          | 0.749 | 0.616                  | 5.3                | 0.999 |
| C.I. Reactive Black 5   | 1.864            | 0.917          | 0.988 | 0.0015                 | 72.2               | 0.924 |
| C.I. Direct Blue 71     | 1.875            | 1.115          | 0.987 | 0.0042                 | 58.7               | 0.978 |
Table 6: Comparison of acid, reactive and direct dyes uptake by silica type adsorbents.

| Dye                                | Silica modifier | Sorption conditions | pH | T (°C) | Additional information |
|------------------------------------|-----------------|---------------------|-----|--------|------------------------|
| C.I. Acid Orange 10                | (3-aminopropyl)triethoxysilane | 35.5-58.1           | 3   | 25-40  | m=0.1 g; v=10 mL        | [24] |
| C.I. Acid Orange 12                |                 | 14.3-19.6           | 1   | 25-40  |                        |     |
| C.I. Acid Red 14                   |                 | 434                 |     |        |                        |     |
| C.I. Acid Black 5                  |                 | 250                 | 2   | 25     | m=0.07 g; v=250 mL      | [15] |
| C.I. Acid Blue 25                  |                 | 167                 |     |        |                        |     |
| C.I. Reactive Red 239              |                 | 152                 | 2   | 25     | m=0.05 g; v=50 mL       | [25] |
| C.I. Acid Orange 7                 |                 | 5.3                 |     |        |                        |     |
| C.I. Reactive Black 5              |                 | 58.7                | 4.9 | 25     | m=0.5 g; v=50 mL        |       |
| C.I. Direct Blue 71                |                 | 72.2                |     |        |                        |       |
| C.I. Reactive Yellow               |                 | 21.1-30.5           | 4   | 25-55  | m=0.1 g; v=50 mL        | [26] |
| C.I. Reactive Red                  |                 | 11.1-14.0           |     |        |                        |     |
| Methyl Orange                      | (3-aminopropyl)trimethoxysilane | 366.6               |     |        |                        |     |
| Orange IV                          |                 | 409.2               | 5.6 | 25     | m=0.02 g; v=10 mL       | [27] |
| Reactive Brilliant Red X3B         |                 | 269.2               |     |        |                        |     |
| Acid Fuchsin                       |                 | 251.8               |     |        |                        |     |
| Rifazol Yellow GR                  | poly(diallydimethyl)ammonium chloride | 365                |     |        |                        |     |
| Rifafix Yellow 3RN 150H            |                 | 287.4               | -   | 25     | m=0.1 g; v=50 mL        | [28] |
| Methylene Blue                     |                 | 138.9               |     |        |                        |     |
| Acidine Orange                     | Fe₃O₄ and —COOH  | 109.8               | 10  | 25     | m=0.01 g; v=10 mL       | [29] |
| Methyl Orange                      | quaternary ammonium polyethylenimine | 112.7              |     |        |                        |     |
|                                    |                 | 105.4               | 7   | 25     | m=0.1 g; v=10 mL        | [14] |

where: m - mass of modified silica, v- volume of dye solution

Figure 4: Equilibrium adsorption data of C.I. Acid Orange 7 (a), C.I. Reactive Black 5 (b) and C.I. Direct Blue 71 (c) on the aminosilane modified silica and the fitting of the Langmuir and Freundlich isotherm model to experimental data (conditions: volume: 50 mL, sorbent mass: 0.5 g, agitation speed: 180 rpm, temperature: 25°C, phase contact time: 60 min).
The adsorption of C.I. Acid Orange 7, C.I. Direct Blue 71 and C.I. Reactive Black 5 dyes can be explained to proceed via the electrostatic attraction between the positively charged protonated amino groups on the silica surface (−NH\(_3^+\)) and the negatively charged sulfonic groups (SO\(_3^-\)) of the dyes:

Silica-NH\(_3^+\) + H\(^+\) → Silica-NH\(_4^+\)

Silica-NH\(_4^+\) + Dye-SO\(_3^-\) → Silica-NH\(_4^+\)-O\(_3^-\)S-Dye.

Fig. 5 illustrates the sorption mechanism of C.I. Direct Blue 71 dye on the surface of aminosilane modified silica in acidic medium. There is noticeable correlation between the size of the dye and the efficiency of its adsorption. The hindrance for adsorption of molecules on the aminosilane modified silica was more distinct with the smallest dye.
molecules of C.I. Acid Orange 7. Furthermore, it is worth noticing that this dye has only two ionic groups (−OH and −SO\(_3^−\) Na) compared with larger C.I. Reactive Black 5 and C.I. Direct Blue 71, which contain more than four ionic groups (−OH, −SO\(_3^−\)Na, −NH\(_2^−\)). The steric effect could hinder the interactions of the sulfonic groups of the dyes with the binding sites of the aminosilane modified silica as the dyes used possess almost flat spatial structure. For example, the reaction taking place on the surface of silica modified with (3-aminopropyl)triethoxysilane with fluorescein resulted in the formation of covalent bonds between the reagents, which may involve formation of hydrogen bonds, van der Waals or electrostatic interactions [31].

### 3.3 Influence of salt and surfactant presence on sorption capacities

Water is a main bath component in the chemical treatment of textiles, and is characterized by the highest surface tension in air at normal temperature (except liquid metals). Reduction of water surface tension by the addition of surfactants is necessary to wet the textile surface, thus facilitating the contact of dissolved dye with the textile. Surfactants are therefore present in wastewaters. Different kinds of surfactants are used to modify the surface properties of materials, such as their surface charge or hydrophobicity/hydrophilicity. In this way, the sorption of organic compounds like dyes can be supported (coadsorption), or even the sorption of normally non-retained species may be enabled (adsolubilization) [32]. However, prediction of the effects of surfactants on dye sorption is not easy, as several simultaneous and competitive mechanisms may be operating during the sorption process [32].

Fig. 6 illustrates the possible interactions that occur between the aminosilane modified silica and dyes in the presence of anionic surfactant in acidic medium. The influence of the anionic surfactant (SDS) on dye sorption was investigated in a system containing 100 mg L\(^{-1}\) of dye and 0.11 g L\(^{-1}\)of SDS. The equilibrium sorption capacities of the aminosilane modified silica decrease with increasing concentration of SDS. The amounts of C.I. Acid Orange 7, C.I. Reactive Black 5 and C.I. Direct Blue 71 retained by the sorbent at equilibrium dropped from 8.0 to 4.05 mg g\(^{-1}\), from 10 to 0.32 mg g\(^{-1}\) and from 10 to 2.1 mg g\(^{-1}\), respectively, with increasing amounts of SDS (Fig. 7a). The SDS surfactant with the same charge as the acid, reactive and direct dyes exhibited a negative effect on dye retention on the aminosilane modified silica due to the competition for adsorption sites.

The presence of inorganic electrolytes such as NaCl or Na\(_2\)SO\(_4\) decreases the surface tension of water negligibly and primarily affects the degree of binding of the dye with the fiber and the stability of colorization. Inorganic auxiliaries enter sewage systems in the amounts they were used in the dyeing bath because they do not deposit on the textile, but only assure a suitable reaction medium. Therefore, it is useful to investigate the effect of various salts on dye adsorption on the adsorbent. The effect of salt addition on dye uptake was studied for a system containing 100 mg L\(^{-1}\) of dye and different amounts of NaCl (from 1 to 25 g L\(^{-1}\)). It was observed that the addition of NaCl in the amounts of 50, 75 and 100 g L\(^{-1}\) to the dye solution of 100 mg L\(^{-1}\) initial concentration caused dye precipitation. As presented in Fig. 7(b) the retention of C.I. Acid Orange 7 and C.I. Reactive Black 5 was reduced in the presence of sodium chloride. A decrease of the amounts of acid and reactive dyes adsorbed at equilibrium was observed from 8.0 to 6.3 mg g\(^{-1}\) and from 10 to 7.8 mg g\(^{-1}\) with increasing amount of NaCl from 1 to 25 g L\(^{-1}\). It can be surmised that chloride anions slightly compete with SO\(_3^−\) groups in dye molecules for adsorption sites on the silica surface. Since dye molecules, which are larger than chloride anions, cannot penetrate the pores easily, the overall result is a lower adsorption capacity. The same effect of NaCl presence on C.I. Acid Orange 10, C.I. Acid Red 14, C.I. Acid Black 1 and C.I. Acid Blue 25 removal using the aminosilane modified silica was described by Donia et al. [26] and Mahmoodi et al. [15]. Qin et al. [27] observed that sorption of four anionic dyes such as Methyl Orange, Orange IV, Reactive Brilliant Red X3B and Acid Fuchsine on on MCM-41 modified by 3-aminopropyltrimethoxysilane was suppressed by less than 15% in the presence of chloride anions.

### 4 Conclusions

Aminosilane modified silica was used as a low cost sorbent for the removal of textile dyes such as Acid Orange 7, C.I. Reactive Black 5 and C.I. Direct Blue 71 from aqueous solution and wastewaters. A satisfactory agreement of the experimental data with the pseudo second-order kinetic model was observed. The affinity sequence of the dyes for the prepared sorbent was as follows: C.I. Reactive Black 5 > C.I. Direct Blue 71> C.I. Acid Orange 7. It seems that aminosilane modified silica can be a promising sorbent for C.I. Reactive Black 5 and C.I. Direct Blue 71 removal from the aqueous solution because of high values of the monolayer capacities (72.2 mg g\(^{-1}\) for C.I. Reactive Black 5...
and 58.7 mg g⁻¹ for C.I. Direct Blue 71). The results indicate that the presence of NaCl does not play a significant role in the reactive and direct dye adsorption. Anionic surfactants reduce sorption capacities. Decolourization of raw wastewaters, originating from the dye bath containing the C.I. Reactive Black 5 dye, was observed after 1 min of phase contact time. For sewages, purification yield was found to be 88.5%. The presented sorption method is appropriate and economical for the removal of reactive and direct dyes from industrial wastewaters.

**Figure 6:** Possible interactions between dye (e.g. C.I. Reactive Black 5 or C.I. Direct Blue 71) and aminosilane modified silica in the presence of anionic surfactant in acidic medium.

**Figure 7:** Effect of SDS (a) and NaCl (b) addition on the dyes sorption at equilibrium by the aminosilane modified silica (conditions: initial dyes concentration: 100 mg L⁻¹, volume: 50 mL, sorbent mass: 0.5 g, agitation speed: 180 rpm, temperature: 25°C, phase contact time: 60 min).
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