

Basic dye removal from aqueous solutions by dodecylsulfate- and dodecyl benzene sulfonate-intercalated hydrotalcite

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Abstract

Dodecylsulfate- and dodecyl benzene sulfonate-hydrotalcites were prepared by calcination–rehydration method. The surfactants intercalation in the interlayer space of hydrotalcite were checked by PXRD and FTIR spectroscopy where the resulting materials were found to be similar to those reported in the literature and were used to remove a basic dye (safranine) from aqueous solutions. The sorption kinetics data fitted the pseudo second order model. The isotherms were established and the parameters calculated. The sorption data fitted the Langmuir model with good values of the determination coefficient. The thermodynamic parameters calculated from Van't Hoff plots gave a low value of ΔG° ($< -20 \text{ kJ mol}^{-1}$) indicating a spontaneous physisorption process. Two regeneration cycles were processed by acetone extraction leading to the same removal capacity of the obtained materials as the original surfactant-intercalated hydrotalcites. The UV–vis spectra of the recovered extracts were similar to the spectrum of safranine, which means that the dye was recovered without any modification.

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1. Introduction

Layered double hydroxides (LDH), which are referred to as hydrotalcite-like compounds (HT) or as anionic clays, are an important class of ionic lamellar solids [1]. They have been widely investigated owing to their potential applications as ion exchangers, catalysts or catalyst supports [2–4]. The structure of LDH consists of positively charged mixed metal hydroxide layers separated by charge-balancing anions and water molecules. The general chemical formula of these lamellar solids can be written as $[\text{M}_{1-x}^{2+}\text{M}_x^{3+}(\text{OH})_2](\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$, where M^{2+} and M^{3+} are divalent and trivalent cations, respectively. These cations occupy the center of $[\text{M}^{2+}/\text{M}^{3+}](\text{OH})_6$ octahedral units and A^{n-} is an organic or inorganic anion. The interesting properties of these materials result from their structural brucite-like sheets. They consist of metal cations octahedrally coordinated to OH^- and an interlayer region containing water and anions which compensate the positive charge of the brucite-like sheets.

Due to their anionic exchange capacity, HT are suitable for sorption of anionic species, but are not applicable for positively charged ones. The synthesis of surfactant-intercalated layered double hydroxides reported in the literature led us to consider this type of materials as sorbent for organic solutes and particularly the positively charged species. The organophilic nature of surfactant in the LDH interlayer would permit the sorption of many types of organic molecules. This way had been extensively used with organic surfactants-intercalated bentonites [5,6]. The surfactant-intercalated hydrotalcites were used to remove pesticides, herbicides and phenols from aqueous solutions [7–10]. However, the removal of cationic organic species from aqueous solutions were not reported elsewhere.

Textile industry wastewater contains a wide variety of toxic dyes, which have a great influence on photosynthetic activity in aquatic biota. Due to their low biodegradability, dyes are generally removed from aqueous solutions by a sorption process using activated carbon [11]. The cost of this process led to numerous studies on alternative removal methods by use of less expensive natural materials and waste by-products such as regenerated spent bleaching earth, sludge, perlite, rice husk, sawdust, ben-

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tonite, organophilic bentonites and layered double hydroxides [12–18].

In the present work, we describe (1) the preparation of dodecylsulfate- and dodecyl benzene sulfonate-intercalated hydrotalcite by the calcinations–rehydration method, using calcined Mg–Al hydrotalcite precursors, (2) the study of the basic dye (safranin) removal process and (3) the regeneration and the reuse of the materials.

2. Experimental

2.1. Starting materials

2.1.1. Hydrotalcite and calcined hydrotalcite

The layered double hydroxide Mg–Al–CO₃, with [Mg]/[Al] ratio equal to 2 was synthesized by co-precipitation at a constant pH of 10, following the method described by Reichle [19]. A mixed solution of 0.1 mol of MgCl₂ and 0.05 mol of Al(NO₃)₃ in 80 ml of distilled water was added dropwise under vigorous stirring to 100 ml of an aqueous solution containing 0.35 mol of NaOH and 0.09 mol of Na₂CO₃. During the co-precipitation process, the pH was maintained at a constant value (10) by addition of 1N HNO₃ solution. The obtained gel is stirred for 20 h at 65 °C until crystallization. The solid was filtered and washed with distilled water until obtaining a Cl[−] free HT-CO₃ (AgNO₃ test). This material was dried at 105 °C for 18 h, ground and finally, 0.250 mm sieved. A fraction of the resulting material was calcined at 500 °C for 4 h. The solid obtained is noted HT-C500.

2.1.2. Surfactant modified hydrotalcite

The surfactants (sodium dodecylsulfate and sodium dodecyl benzene sulfonate) were intercalated by the calcined hydrotalcite rehydration method, which was used in the literature for the insertion of several types of organic molecules [20,21].

An aqueous solution of 1.44 g of sodium dodecylsulfate (SDS) or 5 g of sodium dodecyl benzene sulfonate in 100 ml of distilled water was refluxed for 1 h and then cooled under nitrogen atmosphere. A suspension of 1 g of HT-C500 in the prepared sodium dodecylsulfate or sodium dodecyl benzene sulfonate solution was vigorously stirred for 24 h under nitrogen and centrifuged. The solid was washed three times with hot distilled water, dried at 65 °C for 24 h, crushed and passed through a 0.250 mm sieve. The obtained materials were noted HT-SDS and HT-SDBS for dodecylsulfate- and dodecyl benzene sulfonate-hydrotalcite, respectively.

2.1.3. Characterization of the prepared materials

X-ray powder diffraction data of the hydrotalcite (HT-CO₃), SDS- and SDBS-intercalated hydrotalcite (HT-SDS and HT-SDBS) were collected with monochromatic CuK α radiation using a Phillips PW3710 diffractometer. The IR spectra of the samples in the 4000–400 cm^{−1} were obtained with a FOURIER MATTSON genesis series FTIR spectrophotometer.

2.2. Study of safranin (Saf) removal with HT-SDS and HT-SDBS

2.2.1. Kinetic study

The kinetic study was carried out on HT-SDS and HT-SDBS suspensions in 50 mg/L of safranin solution (solid/solution ratio = 0.5 g/L). Suspensions were stirred for different time intervals (5–360 min) then centrifuged. The dye concentration in the supernatants was measured by visible spectrophotometry on a HACH DR/4000 U spectrophotometer at 518 nm. A six-point calibration curve (5–50 mg/L) was run before each analysis. In this concentration range, the absorbance/concentration curve was linear ($R^2 > 0.99$). The linear Beer–Lambert relationships were used in the concentration analysis. Samples were pH adjusted corresponding to standard conditions. The sorbed amounts were determined from the difference between the initial and final concentrations.

2.2.2. Sorption isotherms

The sorption isotherms were established using HT-SDS and HT-SDBS suspensions in safranin solution (solid/solution ratio = 0.5 g/L) in a range from 5 to 50 mg/L. The suspensions were stirred for 240 min then centrifuged. The safranin equilibrium concentration in the supernatants were determined by visible spectrophotometry at 518 nm.

The sorption capacity of the materials were calculated using the difference between the initial and the equilibrium concentrations (Section 2.2.1).

2.2.3. pH effect on dye removal

This effect was studied on suspensions of HT-SDS and HT-SDBS in 50 mg/L of safranin solution (solid/solution ratio = 0.5 g/L). The pH of the suspensions were adjusted to values in the range from 5 to 8. The suspensions were stirred for 240 min then centrifuged. The dye equilibrium concentration in the supernatants were analysed by visible spectrophotometry at 518 nm as described in Section 2.2.1. The absorbance of the solutions were measured at pH 7.2.

2.2.4. Temperature effect

This effect was studied on suspensions of HT-SDS and HT-SDBS in safranin solutions (50 mg/L dye concentration and 0.5 g/L solid/solution ratio) stirred at three constant temperatures (301, 308 and 318 K) for 4 h. Suspensions were centrifuged; the supernatants were adjusted at pH 7.2 and the equilibrium concentrations were determined by visible spectrophotometry at 518 nm.

2.3. Regeneration of the sorbents

Two regeneration cycles of HT-SDS were performed by acetone extraction of the sorbed dye followed by drying of the solids at 40 °C overnight. The dried solids were used to remove safranin from aqueous solutions at the same solid/solution ratio as in the sorption study (a solid/solution ratio of 0.5 g/L and an initial concentration of 25 mg/L).

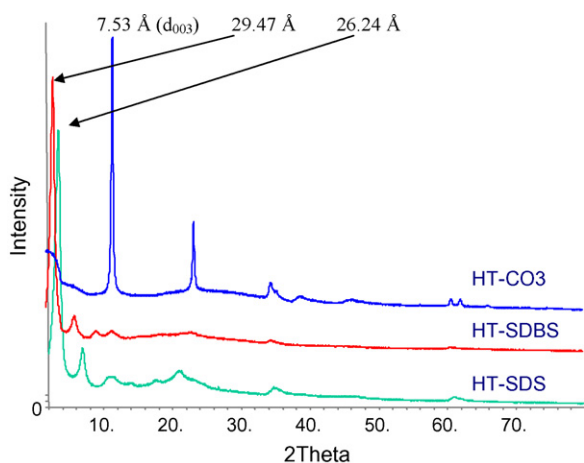


Fig. 1. X-ray powder diffraction patterns of Mg–Al hydrotalcite (HT- CO_3), dodecylsulfate-intercalated hydrotalcite (HT-SDS) and dodecyl benzene sulfonate-intercalated hydrotalcite (HT-SDBS).

The acetone was removed from the extracts by evaporation and the obtained residue was dissolved in distilled water. The UV–vis spectra of the obtained aqueous solutions were recorded in the wavelength range from 200 to 650 nm.

3. Results and discussion

3.1. Characterization of materials

The X-ray powder diffraction pattern of HT- CO_3 (Fig. 1) shows peaks at 7.58 Å (d_{003}), 3.78 Å (d_{006}), 2.58 Å (d_{012}), 1.52 Å (d_{110}) and 1.49 Å (d_{113}), which is similar to those reported by several authors [22–24]. However, the HT-SDS and HT-SDBS diffraction patterns show a shift to 26.24 and 29.47 Å, respectively, indicating the intercalation of the surfactant ions in the hydrotalcite interlayer. The same order of magnitude for these d_{003} values has been reported in the literature [25–27].

The infrared spectrum of HT- CO_3 (Fig. 2) shows the characteristic absorption bands of an hydrotalcite, particularly a broad band at 3421 cm^{-1} (due to the interlayer water molecules)

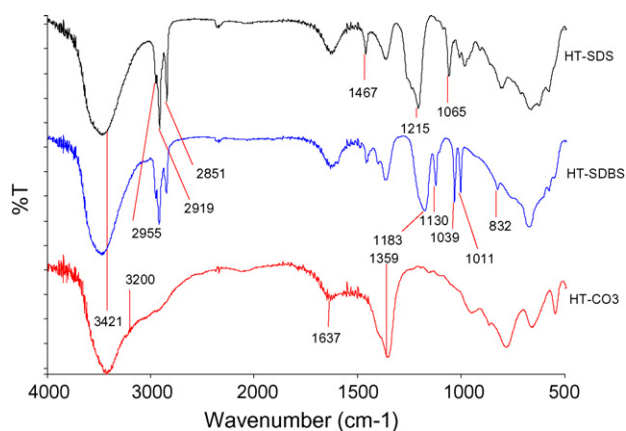


Fig. 2. FTIR spectra of Mg–Al hydrotalcite (HT- CO_3), dodecylsulfate-intercalated hydrotalcite (HT-SDS) and dodecyl benzene sulfonate-intercalated hydrotalcite (HT-SDBS).

with a shoulder near 3200 cm^{-1} (due to the H-bonded stretching vibration). The weak peak at 1637 cm^{-1} can be assigned to the H_2O bending vibration of interlayer water. The strong peak at 1359 cm^{-1} can be assigned to the vibration of carbonate species. The bands in the range of 500–700 cm^{-1} are attributed to metal–oxygen–metal stretching.

The postulated surfactant (SDS and SDBS) intercalation in the hydrotalcite interlayer is confirmed by the infrared spectra of Fig. 2.

The presence of dodecylsulfate ions in the sample is evidenced by the C–H stretching vibration bands 2955, 2919 and 2821 cm^{-1} and a C–H bending vibration band at 1467 cm^{-1} . The sulfate S=O stretching vibration bands at 1215 and 1065 cm^{-1} were also observed.

The infrared spectrum of HT-SDBS (Fig. 2) shows the presence of dodecyl benzene sulfonate ions in the sample. Besides the hydroxyl vibration bands of hydrotalcite and the C–H vibration bands observed in the spectrum of HT-SDS, the HT-SDBS spectrum shows the characteristic vibration bands of the sulfonate group at 1183, 1130, 1039, 1011 and 832 cm^{-1} . The three spectra of Fig. 2 are similar to those reported in the literature for the same materials [28,29].

3.2. Study of safranin removal with HT-SDS and HT-SDBS

3.2.1. Contact time effect on dyes sorption

Plots of Fig. 3 show the % safranin removal (Saf) with hydrotalcite (HT), dodecylsulfate-intercalated hydrotalcite (HT-SDS) and dodecyl benzene sulfonate-intercalated hydrotalcite (HT-SDBS) vs. contact time. Sorption equilibrium was reached after 3 h with HT-SDBS and after more than 4 h with HT-SDS. Bruna et al. reported that for carbetamide and metamitron pesticides sorption on SDS-intercalated hydrotalcite, the equilibrium reached after 2 and 8 h, respectively [8]. Moreover, the HT-SDS and HT-SDBS sorption capacities calculated and expressed in percent uptake were respectively 67 and 41% while lower values were observed for HT (less than 10%).

These preliminary results led to deduce that the intercalation of SDS and SDBS in the hydrotalcite affords a better cationic

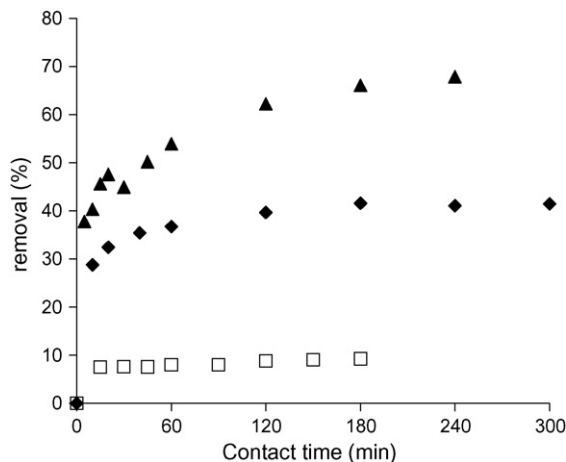


Fig. 3. Effect of contact time on percentage of dye removal by HT- CO_3 (□), HT-SDS (▲) and HT-SDBS (◆) (initial safranin concentration $C_i = 50$ mg/L).

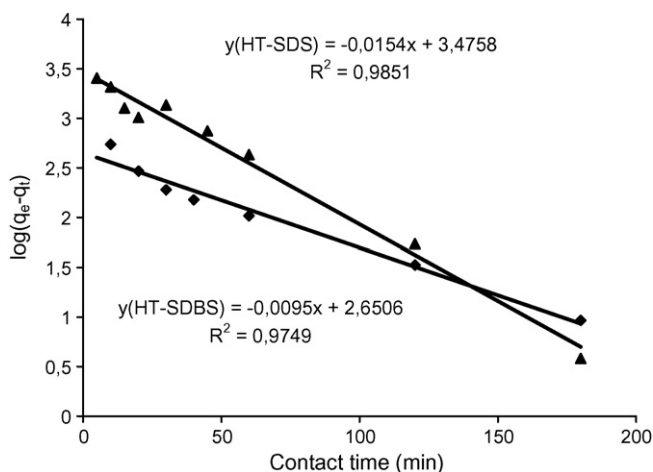


Fig. 4. First order plot for safranin removal from aqueous solutions with HT-SDS (▲) and HT-SDBS (◆) (initial safranin concentration $C_i = 50$ mg/L).

dye sorption capacity. This investigation is only devoted to the HT-SDS and HT-SDBS, which are more efficient than HT in the basic dye removal process.

3.2.2. Kinetic modelling

The sorption kinetics is an important aspect of pollutants removal process control. The Lagergren's first order kinetic model and the Ho's pseudo second order model are the most frequently used in the literature to predict the involved mechanism in the sorption process [30].

The Lagergren's first order model [30] is expressed by the equation:

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (1)$$

where q_t and q_e (mg/g) are respectively the amounts of sorbed dye at time t and at equilibrium and k_1 (min^{-1}) is the first order rate constant. Integration of the Eq. (1) gives:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} \times t \quad (2)$$

Eq. (2) shows a linear relationship between $\log(q_e - q_t)$ and t . Linear regression calculations allow to obtain the values of the rate constant k_1 and the equilibrium removal capacity q_e . These parameters were calculated for the sorption of safranin on HT-SDS and HT-SDBS. The results are plotted in Fig. 4 and the calculated parameters reported in Table 1.

The calculated values from the first order kinetic model show that the experimental results fit this model with determination coefficient values of 0.97 and 0.98 for HT-SDBS and HT-SDS, respectively. Moreover, large differences between experimental

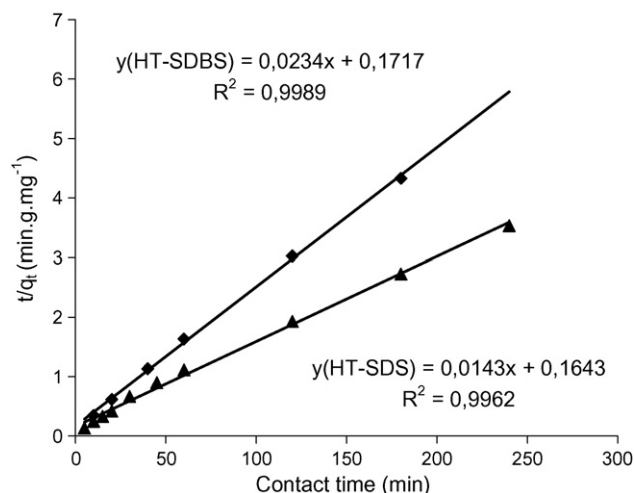


Fig. 5. Pseudo second order plot for safranin removal from aqueous solutions with HT-SDS (▲) and HT-SDBS (◆) (initial safranin concentration $C_i = 50$ mg/L).

and calculated values of the equilibrium sorption capacities are observed (Table 1). We conclude that the first order kinetic model is not adequate to describe the sorption process.

Due to its good correlation with the experimental results, the more recent pseudo second order model has been extensively used by several researchers in the same field [30]. This model is expressed by the Eq. (3):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

where q_t and q_e (mg/g) are respectively the amounts of sorbed dye at time t and at equilibrium and k_2 is the pseudo second order rate constant (g/mg/min).

The integration of Eq. (3) and its linearization gives the expression:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \times t \quad (4)$$

The plots of t/q_t vs. t (Fig. 5) are straight lines where slopes and intercepts are respectively $1/q_e$ and $1/(k_2 q_e^2)$. The values of the rate constant k_2 and of the equilibrium sorption capacity q_e are calculated from these parameters. The calculated k_2 and q_e values and the corresponding linear regression determination coefficient R^2 values for different initial concentrations are reported in Table 1. Good correlation is observed between experimental data and the pseudo second order kinetic model with determination coefficient values higher than 0.99. Values of the rate constant k_2 are of the same order of magnitude as those reported in the literature for the sorption of phenol onto hexadecyl trimethylammonium bentonite [31].

Table 1
Comparison of experimental and calculated values for the first and the second order sorption rate constants

Sorbent	$q_{e,exp}$ (mg/g)	k_1 (min^{-1})	$q_{e,cal}$ (mg/g)	R^2	k_2 (g/mg/min)	$q_{e,cal}$ (mg/g)	R^2
HT-SDBS	44.2	0.0095	14.2	0.975	0.0032	42.7	0.999
HT-SDS	67.9	0.015	32.3	0.985	0.0012	69.9	0.996

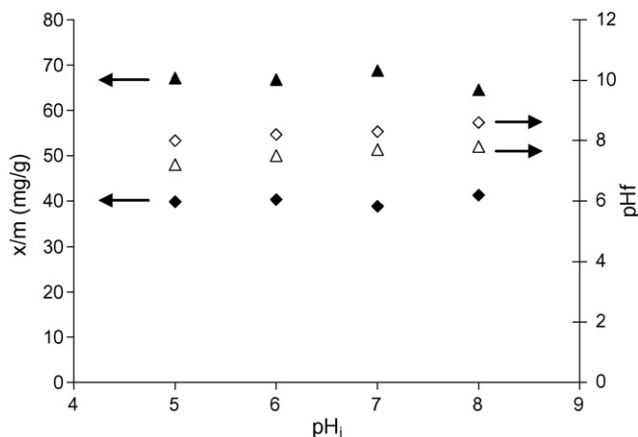


Fig. 6. Effect of initial solution pH on safranin removal from aqueous solutions with HT-SDS (▲) and HT-SDBS (◆).

For both materials, the differences between the experimental and calculated values of the equilibrium removal capacity were lower than 4%.

3.2.3. pH effect on dye removal

Fig. 6 shows the plots of final pH and HT-SDS and HT-SDBS sorption capacity vs. initial pH ranging from 5 to 8. It was observed that the sorption capacity and final pH were practically constant in this initial pH domain. This pH stability is probably due to the buffering properties of hydrotalcite. Similar observation was made in the literature with hydroxide sludge and hydrotalcite [7,32]. This result indicates that HT-SDS and HT-SDBS remove the cationic dye with the same efficiency in this range of pH values.

3.2.4. Sorption isotherms

The equilibrium sorption experimental data obtained in this study were analysed using the commonly used Freundlich and Langmuir isotherm models.

The empirical Freundlich model which is known to be satisfactory for low concentrations is expressed by the equation:

$$q_e = K_F \times C_e^{1/n} \tag{6}$$

where q_e is the equilibrium sorption concentration of solute per gram of adsorbent (mg/g), C_e is the equilibrium aqueous concentration of the solute (mg/L), K_F and n are Freundlich constants which are related to adsorption capacity and intensity of adsorption.

Eq. (6) can be linearized in its logarithmic form, which enables the determination of Freundlich constants as below:

$$\log q_e = \frac{1}{n} \times \log C_e + \log K_F \tag{7}$$

The Langmuir isotherms model is described by the following equation:

$$q_e = \frac{Q_{\max} K_L C_e}{1 + K_L C_e} \tag{8}$$

where q_e (mg/g) is the amount of dye removed per gram of sorbent, Q_{\max} (mg/g) is the maximum sorption capacity, C_e (mg/L)

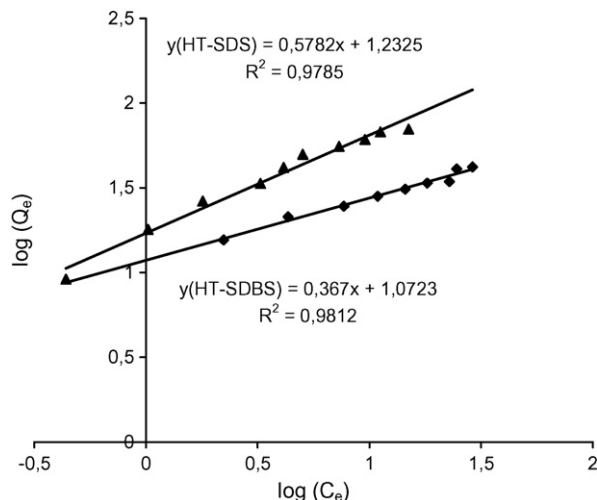


Fig. 7. Freundlich isotherms of safranin removal from aqueous solutions with HT-SDS (▲) and HT-SDBS (◆) (solid solution ratio = 0.5 g/L).

is the dye concentration in the equilibrium solution, and K_L (L/mg) is the Langmuir constant related to the adsorption energy.

For the convenience of plotting and determining the Langmuir constants, the Langmuir equation can be rearranged to linear form as below:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{Q_{\max} K_L} \tag{9}$$

Figs. 7 and 8 show Freundlich and Langmuir isotherms for the safranin sorption on HT-SDS and HT-SDBS. Our experimental results are well described by both models, but the Langmuir model remains the best. The determination coefficient values for this model were higher than those of Freundlich model (0.994 and 0.995 for the Langmuir model against 0.978 and 0.981 with HT-SDS and HT-SDBS, respectively). The calculated parameters of Freundlich and Langmuir are reported in Table 2. The maximal sorption capacity Q_{\max} and the parameter K_L related to adsorption energy are higher for HT-SDS than for HT-SDBS

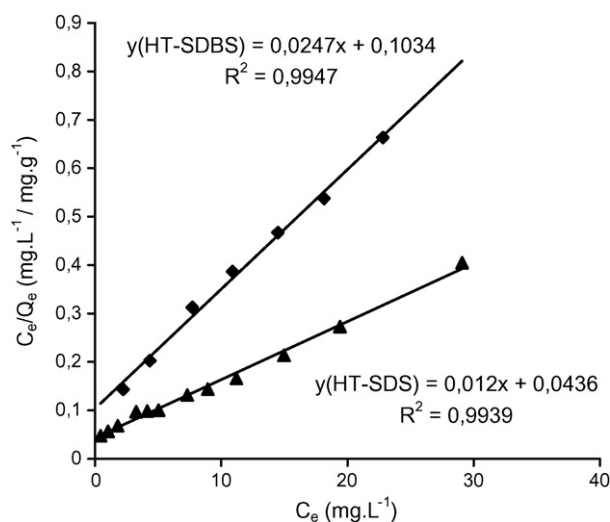


Fig. 8. Langmuir isotherms of safranin removal from aqueous solutions with HT-SDS (▲) and HT-SDBS (◆) (solid solution ratio = 0.5 g/L).

Table 2
Langmuir and Freundlich constants for safranine adsorption on HT-SDS and HT-SDBS

Sorbents	Langmuir constants			Freundlich constants		
	Q_{\max} (mg/g)	K_L (L/mg)	R^2	K_F	n	R^2
HT-SDBS	40.5	0.239	0.995	11.8	2.72	0.981
HT-SDS	83.3	0.275	0.994	17.1	1.73	0.978

(83.3 mg/g and 0.275 for HT-SDS against 40.5 mg/g and 0.239 for HT-SDBS respectively). Lee et al. reported similar magnitude of K_L values (0.155–0.501 L/mg) for crystal violet and phenol red sorption study onto cetylpyridinium montmorillonite [17].

3.2.5. Temperature effect

The study of the temperature effect on safranine removal by HT-SDS and HT-SDBS enabled us to determine the thermodynamic parameters (ΔG° , ΔH° and ΔS°) of these reactions by using the following equation:

$$\ln(K_d) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (10)$$

where R is the ideal gas Constant, T is the temperature (K) and K_d is the distribution coefficient (amount of removed safranine per gram of material divided by its concentration in the liquid phase).

The plot of $\ln(K_d)$ against $1000/T$ gives a straight line, the slope and the intercept correspond to $\Delta H^\circ/R$ and $\Delta S^\circ/R$, respectively.

The plots of $\ln(K_d)$ vs. $1000/T$ for safranine removal with HT-SDS and HT-SDBS (Fig. 9), show a positive slope for both materials.

The thermodynamic parameters calculated from the values of the slopes and the intercepts are reported in Table 3. A negative ΔG° value indicates that the removal process is spontaneous with both materials (HT-SDS and HT-SDBS). ΔS° can be used to describe the randomness at the solid–solution interface during the removal process. As showed in Table 3, the negative values of ΔG° are indications of the spontaneous nature of the removal

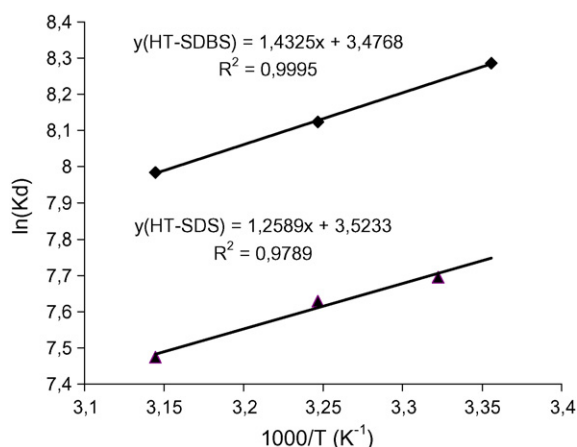


Fig. 9. Plots of $\ln K_d$ vs. $1000/T$ for safranine removal with HT-SDS (\blacktriangle) and HT-SDBS (\blacklozenge).

Table 3
Values of thermodynamic parameters for safranine removal with HT-SDS and HT-SDBS

	ΔS° (J mol ⁻¹ K ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔG° (kJ mol ⁻¹)		
			301 K	308 K	318 K
HT-SDBS	28.9	-11.9	-20.6	-20.8	-21.1
HT-SDS	29.3	-10.5	-19.3	-19.5	-19.8

process with both materials. The low values of ΔG° and ΔH° (<20 kJ mol⁻¹) indicate that the removal process is probably a physisorption [33].

3.3. Regeneration of the sorbents

The safranine sorption efficiency of HT-SDS was tested after two regeneration cycles (Fig. 10). The first and second regenerations of HT-SDS did not affect its dye sorption capacity. The same results were obtained for HT-SDBS. This observation is very important for economical reasons and led to deduce that this sorbent could be reused with the same efficiency.

The integrity of the dye recovered by extraction was verified by the UV–vis spectra (Fig. 11), which were similar to the UV–vis safranine spectrum.

The regeneration of the surfactant-intercalated hydrotalcites without efficiency decrease and the unmodified dye recovery constitute a double economical interest for the use of these materials (Figs. 10 and 11). The hydrotalcite regeneration reported in the literature is a calcination–rehydration process in which the sorbed species were lost during the calcination step and a high decrease (69%) of the removal efficiency

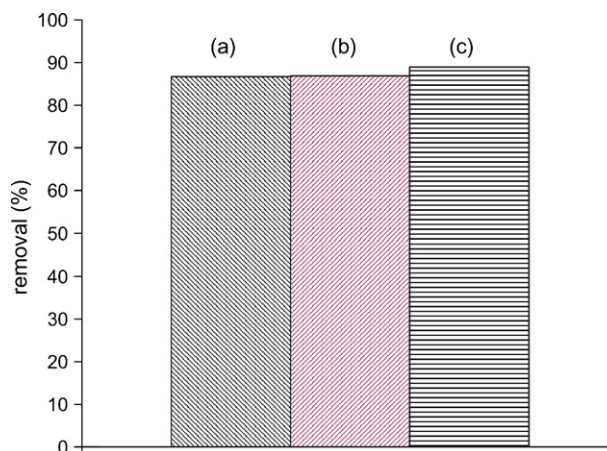


Fig. 10. Comparison of the % safranine sorption with HT-SDS after the first use (a) and two regeneration cycles (b and c).

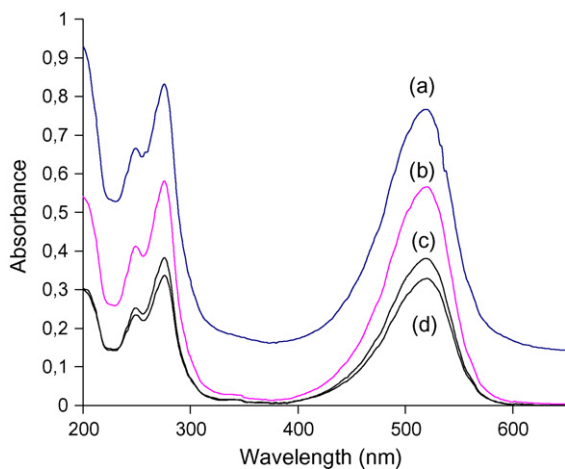


Fig. 11. UV-vis spectra of a safranin aqueous solution (d) and the three extracts obtained after first use (a) and after sorption on regenerated HT-SDS (b and c).

was noticed [18]. The same decrease of the sorption capacity (50%) was reported elsewhere for an hydrotalcite regenerated by calcination–rehydration [20]. In another work with surfactant modified alumina, the dye (crystal violet) was recovered but the sorption efficiency of the material decreased after regeneration [34].

4. Conclusion

In this study, dodecylsulfate and dodecyl benzene sulfonate ions were intercalated in the interlayer space of an hydrotalcite. The obtained materials were characterized and used for a basic dye removal from aqueous solutions. The kinetic and sorption data fitted well the second order kinetic model and the Langmuir model respectively with good values of the determination coefficient. The sorption was found to be a pH independent and a physisorption process.

The safranin extracted with acetone from the used material was recovered without alteration. The regenerated materials were subjected to dye sorption experiments followed by a second regeneration cycle. The obtained results led us to deduce that multiple regeneration cycles were possible without any decrease of the sorption efficiency, and with a quantitative recovery of the sorbed dye. The surfactant modified hydrotalcites are promising reusable materials for removal and recovery of dyes.

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