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Uptake of anionic surfactants from aqueous medium by using porous anionic clays with tailored properties

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ABSTRACT

Layered double hydroxides, containing Mg or Zn as divalent cations in the brucite - like layer and the derived mixed oxides obtained after the calcination process of the clays have been used to remove the anionic surfactant, sodium dodecylbenzenesulfonate, from aqueous solutions. The property of the layered clay to reconstruct its structure by using its structural "memory effect" has been used as a controlled variable parameter during the adsorption/intercalation processes of the tested anionic surfactant. The extent of sodium dodecylbenzenesulfonate removal decreases in the order: 2ZnAlLDH550 > 2MgAlLDH550 > ZnAlLDH550 > MgAlLDH550 > REZnAl550 > REMgAl550 > ZnAlLDH > MgAlLDH. A maximum removal capacity, equal to 847 mg/g, was obtained. The results point out that specific textural features and electrostatic properties of the clay matrices can be used as tailored parameters during the removal process of the anionic surfactants from wastewaters.

Keywords: Anionic surfactant; Anionic clays; Removal capacity

1. Introduction

Anionic surfactants are widely used in our daily life (especially in detergents and cosmetics). Recent research has found that they have accentuated toxic effects on human, animal and marine life health [1,2]. The quantity of the anionic surfactants, we are using, is continuingly increasing thus the contamination of ground and surface water with anionic surfactants becomes a serious environmental problem in both industrial and developing countries. As a consequence, a high interest exists nowadays towards finding low cost, but also human health-friendly materials possessing high removal capacities of anionic surfactants from aqueous mediums.

Hydrotalcite—like anionic clays or, more generally speaking, layered double hydroxides (LDHs) – represented by the empirical formula $[M(II)_{1-x}\ M(III)_x{\cdot}(OH)_2]^{x+}\ (A^{n-}){\cdot}mH_2O$—are synthetic inorganic matrices whose structure can be described as containing brucite ($Mg(OH)_2$)-like layers in which some of the divalent cations have been replaced by trivalent ions, thus resulting in positively charged sheets [3]. The positive charge is balanced by the intercalation of anions in the hydrated interlayer regions. The large variety of the compositions that can be developed by altering the nature of the divalent and trivalent cations (M^{II}, M^{III}), the different nature of the interlayer anions (A^{m-}) and the stoichiometric coefficient (x) give rise to a large diversity of layered anionic clay – like structures owning not only high anionic exchange, but also tailored textural properties; this features emerges a porous layered matrix with high adsorption

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capacity [4,5]. The thermal treatment of the substituted hydrotalcites gives rise to bifunctional mixed oxides that are defined by a unique combination of acid-base-redox properties and a large surface area [3]. LDHs and the derived mixed oxides have been already studied as potential adsorbents for removing toxic anionic species [6–8].

Considering all this information, we have prepared LDH-like materials with specific textural and electrostatic properties to be tested in the removal process of sodium dodecylbenzenesulfonate (denoted as AS)—as a representative of anionic surfactants—from the aqueous medium. We present here new results regarding the performance of LDH clays, with Mg and Zn as divalent cations in the brucite—like layer, in the process of removal of AS from aqueous solutions as a function of a tailored calcination treatment of the clay matrix.

2. Experimental

2.1. Synthesis of LDHs samples

The hydrotalcite-like samples were synthesized following the standard aqueous precipitation method of Reichle [9] under a bubbling constant flow of nitrogen in the reaction medium [5] and vigorous stirring.

MgAlLDH: 100 ml of an aqueous solution of $Mg(NO_3)_2 \cdot 6H_2O$ (0.02 mol)/$Al(NO_3)_3 \cdot 9H_2O$ (0.01 mol) and an aqueous solution of $NaOH/Na_2CO_3$ were added dropwise together in such a way that the pH remained at a constant value of 10.5. ZnAlLDH: the precipitants $NaOH/Na_2CO_3$ and 100 ml of an aqueous solution containing $Zn(NO_3)_2 \cdot 6H_2O$ (0.02 mol)/$Al(NO_3)_3 \cdot 9H_2O$ (0.01 mol) were added dropwise together; the pH of the synthesis medium was kept at a constant value of 9.1 ± 0.2. The resulting solids were aged at 65 °C for 14 h, washed three times with deionized water and dried at 110°C overnight. After the calcination in air at 550 °C, for 20 h, with a heating rate of 8 $K \cdot min^{-1}$, the calcined samples are denoted as MgAlLDH550 and ZnAlLDH550, respectively.

The structural "memory effect" of the LDH was used to reconstruct the layered anionic clay network by adding the calcined samples to an aqueous solution of Na_2CO_3 (0.1 M), under stirring, for 7 h. The reconstructed samples were denoted after the calcination treatment at 550 °C as 2MgAlLDH550 and 2ZnAlLDH550 respectively. Sodium dodecylbenzenesulfonate were commercially obtained from Aldrich. The removal of AS from the aqueous medium was conducted in suitable closed flasks of 500 ml volume, at 27 ± 2 °C, under magnetic stirring, for 36 h. 1.0 g of fresh calcined or as—synthesized clay were added to the solution of AS with concentration within the range (0.5×10^{-3}–0.5×10^{-1}) mol/l. After 36 h the suspensions were centrifuged and the supernatant was filtered. The resulting LDH-hybrids, denoted as ASMgAlLDH and ASZnAlLDH, were calcined at 550 °C for 10 h and reused in a new removal procedure of AS; these samples are denoted as REMgAl550 and REZnAl550 respectively. The amount of the anionic surfactant in the filtrate was analyzed spectrophotometrically, at 654 nm, by using the method reported by Koga et al. [10]. The quantity of the removed AS was calculated by difference expressed as percentage removal and denoted as AS_R (%).

2.2. Characterisation of the studied samples

X-ray fluorescence spectroscopy (XRF), Shimadzu XRF-1700 sequential XRF spectrometer, was used to determine the Me^{2+}/Me^{3+} atomic ratios of the samples. Powder X-ray diffraction (XRD) patterns were recorded using a Philips PW 1840 diffractometer under the following conditions: 40 kV, 30 mA, monochromatic CuKα radiation (λ = 0.15418 nm) over a 2θ range from 4 to 70°. The nitrogen adsorption—desorption isotherms were recorded at 77 K on a Coulter SA 3100 automated gas adsorption system on samples previously degassed at 383 K for 7 h under vacuum. Specific surface areas (S_{BET}) were determined using the Brunauer-Emmett-Teller (BET) method on the basis of adsorption data. A Jasco UV-VIS V550 spectrophotometer was used for the UV-VIS analysis.

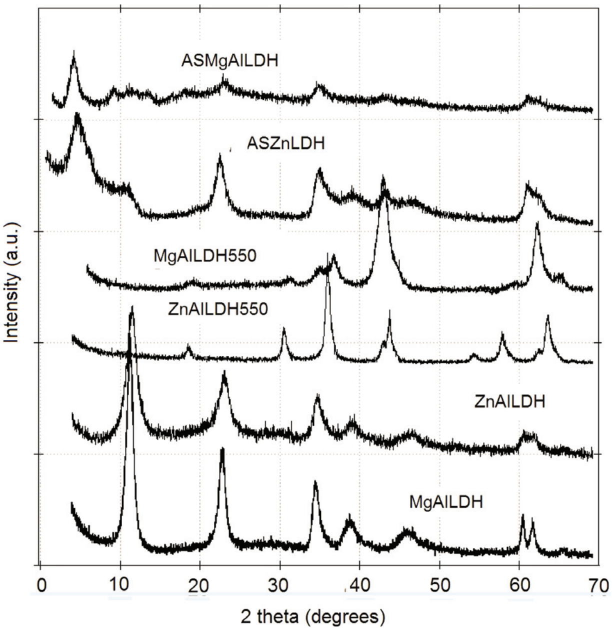

Fig. 1. XRD patterns of the studied samples.

3. Results and discussions

The powder XRD patterns of the tested samples are shown in Fig. 1. The characteristic reflections are indexed to a hexagonal lattice with R-3m rombohedral symmetry, commonly used for the description of hydrotalcite-like anionic clays. For the anionic clays—like samples, the main diffraction peaks of the hydrotalcite structure [4] with a series of (*001*) peaks, which are sharp and symmetric at a low 2θ angle, but broad and asymmetric at a high 2θ angle, are clearly observed. For the AS incorporated clays, ASMgAlLDH and ASZnAlLDH, the first peak, ascribed to diffraction by planes (*003*), is shifted at lower 2θ angles. If the width of the brucite-like layer (0.48 nm [4]) is subtracted, the resulted gallery heights are equal to 1.76 and 1.74 nm. This indicates that the clay layers expand and the anionic surfactant is incorporated in the clay interlayer. After calcination at 550 °C, the layered LDH structure completely collapses and the new reflections indicate the formation of poorly crystallized mixed oxides [3]. The textural properties are important features for establishing the adsorption characteristics of a material. As a consequence, the textural properties of the samples were studied by using N_2 adsorption. Table 1 shows the values of BET surface area (S_{BET}) and pore volume (V_p) of the samples. The S_{BET} is equal to 94 m^2/g and 81 m^2/g for the as-synthesized clays; after the thermal treatment, the corresponding value reaches 152 m^2/g and 129 m^2/g for MgAlLDH550 and ZnAlLDH550, respectively. The adsorption/intercalation process of AS gives rise to a strong decrease in the surface area equal to 37 m^2/g for MgAlLDH and 27 m^2/g for ZnAlLDH; this result is in agreement with the previous reported studies regarding LDHs hybrid materials [11,12]. Superior values of surface area are obtained after the second cycle of calcination process; the maximum, equal to 197 m^2/g, is reached for 2MgAlLDH550. The pore volume values of the calcined clays are also increasing. AS incorporation gives rise to a slight decrease in S_{BET} and V_p, revealing a nonporous state for ASMgAlLDH and ASZnAlLDH. The performance of the tested samples in the process of sodium dodecylbenzenesulfonate removal from an aqueous medium is presented in Fig. 2. The as-synthesized clays show a low removal capacity for AS from the aqueous medium equal to nearly 15% and 21% for MgAlLDH and ZnAlLDH respectively. The AS_R (%) increases to 68% for MgAlLDH550 and to 75% for ZnAlLDH550. The calcination process destroys the brucite-like layered structure of the clay and low crystallized mixed oxides emerge [13] thus a combined sorption—intercalation process contribute to enhance the ability of the mixed oxides for AS removal from aqueous medium. A tailored calcination—reconstruction (in the presence of CO_3^{2-})—calcination cycle of the clay gives rise to a slight increase in the AS removal with AS_R value equal to 87% for 2MgAlLDH550. The maximum value, equal to 95%, is obtained for 2ZnAlLDH550. The result can not be explained by considering only the maximum values of the surface area and pore volume of 2MgAlLDH550 considering that that Zn containing samples have a higher removal capacity of AS in comparison to the Mg containing samples. The specific composition (giving specific electrostatic interactions inside the clay matrix) and the specific textural characteristics both contribute to establish the performances of the adsorption/intercalation process of AS in the derived anionic clay matrices. For an adsorbent the re-use is economically

Table 1

The nomenclature of the studied samples, the BET surface area and pore volume obtained from N_2 adsorption data and the characteristic interlayer free space (IFS)

Sample	Me^{2+}: Me^{3+}	S_{BET} (m^2/g)	V_p (ml/g)	IFS* (nm)
MgAlLDH	2.0	94	0.347	0.29
ZnAlLDH	1.9	81	0.340	0.34
ASMgAlLDH	2.0	37	–	1.76
ASZnAlLDH	1.9	27	–	1.74
MgAlLDH550	2.1	152	0.359	–
ZnAlLDH550	2.1	129	0.354	–
2MgAlLDH550	2.1	197	0.370	–
2ZnAlLDH550	2.0	151	0.361	–
REMgAl550	n.d.	41	–	–
REZnAl550	n.d.	31	–	–

*Interlayer free space, IFS = d_{003}–0.48 nm.

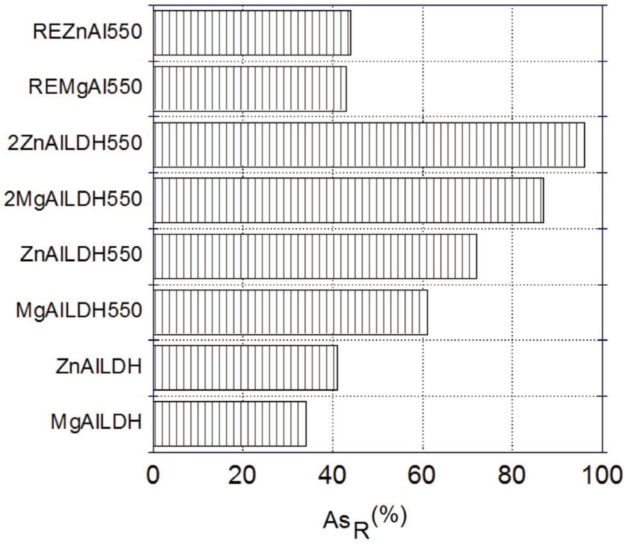

Fig. 2. The anionic surfactant removal capacity (AS_R) of the tested samples from the aqueous solution of AS (V = 500 ml, pH = 6.0, T = 28 °C, $w_{adsorbent}$ = 1 g).

important. A special characteristic of LDHs materials is the “so-called” anionic clay structural “memory effect”. This means that the layered clay structure can be destroyed by calcination at moderated temperatures (~500 °C) to yield low-crystalline mixed oxides and then reconstructed by treatment with aqueous solutions containing anionic species [7]. Calcination of ASLDHs hybrids involves the combustion of the adsorbed organic pollutant therefore the resulted materials, can be reused. The reused samples (denoted as ReLDHs) are the result of the following cycle: calcination-AS adsorption-calcination; their removal capacity of AS, expressed as AS_R (%), decreases to almost 35%. This result points out that after one adsorption cycle the AS removal capacity of the LDHs derived materials decreased. Sorption isotherm of AS by 2ZnAlLDH550 (the adsorbent mass was equal to 0.4 g) is presented in Fig. 3. The isotherm is modelled by the commonly used isotherm equations, Langmuir (Eq. 1) and Freundlich (Eq. 2) [14].

$$1/Q_E = 1/C_L Q_m C_e + 1/Q_\mathrm{m} \tag{1}$$

$$Q_E = C_F \cdot C_e^{\,n} \tag{2}$$

where Q_E (mg /g) is the amount of AS removed at equilibrium and Q_m is the theoretical maximum sorption capacity of the monolayer, C_F and C_L are the empirical constants and C_e (mg/l) is the equilibrium concentration of AS in the tested aqueous medium. The calculated correction coefficient (R^2), of Langmuir and Freundlich isotherms, is equal to 0.899 and 0.937, respectively; this indicates that data for AS sorption by 2ZnAlLDH are better fitted by the Freundlich equation than by the Langmuir equation [15].

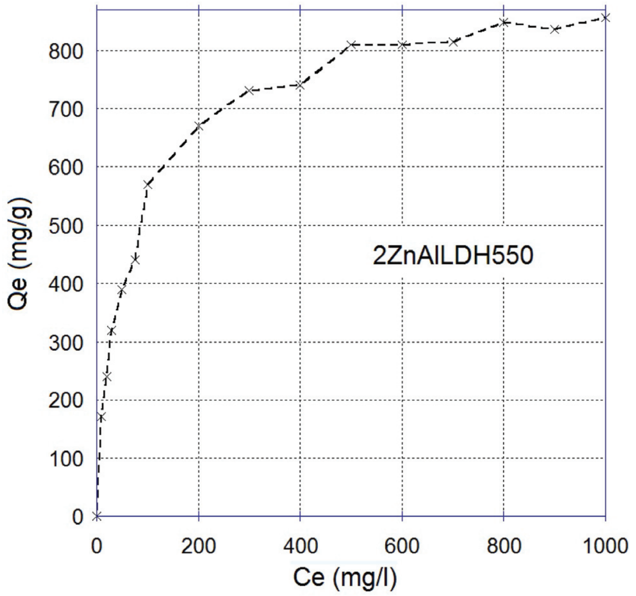

Fig. 3. Sorption isotherm for AS by 2ZnAlLDH550 (V = 100 ml, pH = 6.0, T = 28 °C, $w_\mathrm{adsorbent}$ = 0.4 g).

4. Conclusion

Synthetic anionic clays, type MgAlLDH and ZnAlLDH, are synthesized and tested in the removal process of sodium dodecylbenzenesulfonate from the aqueous solutions. Both the thermal treatment procedures of the clay and its specific composition contribute to establish particular textural and electrostatic properties of the tested samples. A maximum value of the AS_R(%), equal to nearly 95%, is characteristic for the sample obtained after a calcination-reconstruction (in the presence of CO_3^{2-})—calcination procedure of Zn substituted hydrotalcite. After one adsorption cycle the removal capacity of the calcined LDHs decreases.

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