Optimization of layered double hydroxide stability and adsorption capacity for anionic surfactants

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Abstract Low cost adsorption technology offers high potential to clean up laundry rinsing water. From an earlier selection of adsorbents (Schouten et al. 2007), layered double hydroxide (LDH) proved to be an interesting material for the removal of anionic surfactant, linear alkyl benzene sulfonate (LAS) which is the main contaminant in rinsing water. The main research question was to identify the effect of process parameters of the LDH synthesis on the stability of the LDH structure and the adsorption capacity of LAS. LDH was synthesized with the co-precipitation method of Reichle (1986); a solution of $M^{2+}(NO_3)_2$ and $M^{3+}(NO_3)_3$ and a second solution of NaOH and Na_2CO_3 were pumped in a beaker and mixed. The precipitate that was formed was allowed to age and was subsequently washed, dried and calcined. The process parameters that were investigated are the concentration of the initial solutions, M^{2+}/M^{3+} ratio and type of cations. The crystallinity can be improved by decreasing the concentration of the initial solutions; this also decreases the leaching of M^{3+} from the brucite-like structure into the water. The highest adsorption capacity is obtained for Mg^{2+}/Al^{3+} with a ratio 1 and 2 because of the higher charge density compared to ratio 3. Storing the LDH samples in water resulted in a reduction of adsorption capacity and a decrease in surface area and pore volume. Therefore, LDH is not applicable in a small device for long term use in aqueous surroundings. The adsorption capacity can be maintained during storage in a dry N_2 atmosphere.

Keywords Layered double hydroxide · Stability · Anionic surfactant · Adsorption capacity

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1 Introduction

Recycling of water is crucial in times of water scarcity. In developing countries typically half of the daily amount of water is used for doing laundry. Laundry rinsing water is relatively clean and therefore highly suitable for water re-use. To re-use the rinsing water, the main contaminants need to be removed such as the added detergent ingredients and "dirt" constituents released from the fabrics during rinsing. In this paper we focus on removing the main component of detergents, namely the surfactants. The conventional methods for surfactant removal from water involve processes such as chemical and electrochemical oxidation, membrane technology, chemical precipitation, photo-catalytic degradation, adsorption and various biological methods (Holmberg et al. 2003; Adak et al. 2005). Many of these processes are not cost effective and/or not suitable for application on a household scale. However, adsorption technology can be applied in small devices, is applicable on household scale and therefore has the potential to become a suitable low-cost technology. From a previous investigation (Schouten et al. 2007) layered double hydroxide (LDH) proved to be a suitable material for the adsorption of anionic surfactants. The adsorption capacity was found to

Fig. 1 Schematic representation of the co-precipitation method of LDH and the main process parameters investigated. Samples are taken at point *3*, precipitated LDH (*PLDH*), point *6* aged LDH (*ALDH*) and point *7*, calcined LDH (*CLDH*)
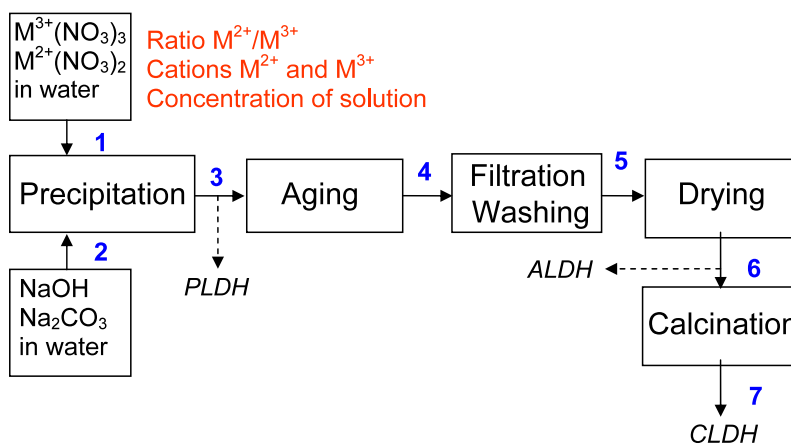
be very high: 1400 mgLAS/gLDH at typical surfactant concentrations found in rinsing water (0.2 g LAS per kg water Ramakrishnan 2004). LAS is linear alkyl benzene sulfonate, which is predominantly used in detergents. The high adsorption capacity compared to the relatively low cost make LDH an interesting material for further research.

Layered double hydroxides derive their name from their structure. They consist of two brucite like layers; sheets of octahedrons of magnesium hydroxide. If a magnesium cation is replaced by an aluminium cation, the layer will be charged positive. In order to balance the residual charge, anions are intercalated between the layers. The general formula of a LDH is: $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+} X^{m-}_{x/m} \cdot nH_2O$, where M^{2+} represents the bivalent cation, M^{3+} the trivalent cation, X^{m-} the intercalated anion with $m-$ charge and n is the number of water molecules. An LDH that can be found in nature is hydrotalcite ($[Mg_6Al_2(OH)_{16}](CO_3^{2-}) \cdot 4H_2O$) although it is rare. Fortunately, LDH is commercially available at large quantities and low cost (Pringadi 2005).

There are several methods to produce LDHs. Reichle (1986) reported co-precipitation as an easy and efficient method to prepare large amounts of LDH. Figure 1 shows the co-precipitation process schematically with the main process parameters and process steps. The M^{2+}/M^{3+} ratio influences the amount of positive charges. A low M^{2+}/M^{3+} ratio indicates a high M^{3+} content and a high charge density. Ratios between 2 and 4 resulted in LDH only; other ratios resulted partly in a LDH and other metal oxides. Cations M^{2+} and M^{3+} having an ionic radius not too different from that of Mg^{2+} can form an LDH (Reichle 1986). The concentration of initial solutions will influence the size and crystallinity of the nanoparticles. Low saturation conditions usually increase crystallinity compared to higher saturation conditions. In the latter situation the nucleation rate is higher than the rate of crystal growth and this result in a large number of small crystallites (Cavani et al. 1991).

Each production step influences the properties of the final product. Aging will increase the crystallinity (Cavani

et al. 1991). Reichle (1986) and Ulibarri et al. (1995) reported a high surface area and more crystalline materials at aging temperatures of 60 to 80 °C. Washing is essential to remove unreacted reagents. During calcination the water molecules between the layers will be removed and the CO_3^{2-} is converted to CO_2. The CO_2 eludes and leaves a porous structure behind (Ulibarri et al. 1995). Furthermore, the hydroxyl groups of the brucite structure will be converted to oxide groups resulting in a mixed metal oxide. An important property of the calcined LDH is the memory effect; in aquatic environments it can easily return to its original layered structure (Ulibarri et al. 1995; Pavlovic et al. 2005; Zhu et al. 2005).

Because of their structure LDHs can exchange intercalated anions and can be applied in broad areas as adsorbents, catalysts, anion exchangers, acid residue scavengers, and antacids in the medical field (Reichle 1986). Adsorption of different adsorbates is often studied and reported; examples are arsenates (Lazaridis et al. 2002), chromates (Lazaridis et al. 2001; Lazaridis and Asouhidou 2003), acidic pesticides (Pavlovic et al. 2005), phenols (Ulibarri et al. 1995), anionic dyes (Zhu et al. 2005) and phosphorus contaminates (Shin et al. 1996). Pavan et al. (1998, 1999, 2000), Kopka et al. (1988), Anbarasan et al. (2005) and Reis et al. (2004) investigated the adsorption of anionic surfactants on LDH. The adsorption of anionic surfactants takes place on the external surface area as well as intercalated in the LDH, which is also described in Pavan et al. (2000), Kopka et al. (1988), Anbarasan et al. (2005). However, no studies were reported on the effect of synthesis parameters of LDH on the adsorption capacity for anionic surfactants and the stability of such materials.

In the application under investigation, we aim to apply LDH small household scale devices. Assuming that this device will be used for several months, the LDH stability is important during that period. The adsorption capacity should remain both during storage and use, where the latter means in aquatic surroundings. The objective of this study is to

identify the effect of process parameters for LDH synthesis and storage on the LDH structure, stability and adsorption capacity for LAS. To investigate the best storage method to maintain the stability, the LDH samples are stored in different atmospheres, such as dry N_2 (exclusion of CO_2), dry air, open air, a vial and in water. The process parameters that are varied are the M^{2+}/M^{3+} ratio, type of cations and concentration of initial solutions. Furthermore, the influence of aging and calcination is studied. The LDH was characterized (surface area and pore volume) and its LAS adsorption capacity was measured after each step.

2 Materials and methods

2.1 Materials

Magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$), aluminium nitrate ($Al(NO_3)_2 \cdot 9H_2O$), zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$), iron nitrate ($Fe(NO_3)_2 \cdot 9H_2O$), sodium carbonate (Na_2CO_3) and sodium hydroxide (NaOH) are analytically pure reagents and obtained from Boom (Meppel, The Netherlands), Merck (Darmstadt, Germany) and Sigma-Aldrich (Steinheim, Germany). Anionic surfactant, linear alkyl benzene sulfonate (LAS), was obtained from Unilever R&D, Vlaardingen, The Netherlands. Purity is around 92 wt%. The chain length of LAS is C10 to C13 (equal distributed, average molecular weight of LAS-acid is 312 g/mol).

2.2 Preparation of LDH

The concentration of the initial solutions, M^{2+}/M^{3+} ratios and aging are expected to influence the crystallinity. The concentration of the aluminium nitrate solution was taken at the saturation point (HC: high concentration) and at 50% of the saturation point (LC: low concentration). For a given ratio the concentration of the magnesium nitrate solution is fixed. Ratios investigated are 1.5, 2 and 3 (mol ratio). Ratio 4 is not used, because a high charge density is preferred to obtain a high adsorption capacity. Ratio 1.5 is investigated to understand the influence of charge density and the possible production of other metal oxides. The influence of aging and calcination is studied by taking samples at different points in the production process, which is shown in Fig. 1; point 3, precipitated LDH (PLDH), point 6, aged LDH (ALDH) and point 7, calcined LDH (CLDH). The sample taken at point 3 is immediately washed and dried to investigate the effect of aging. Four cations were investigated: magnesium (Mg^{2+}), aluminium (Al^{3+}), zinc (Zn^{2+}) and iron (Fe^{3+}). Combinations with other metal ions were not investigated because either the production process becomes too complicated, or no LDH is formed or leaching of one of the cations would result

in hazardous contamination of the cleaned water. The carbonate anion is used to produce an open structure after calcination. Mg and Al are used to find the optimal production method with the highest adsorption capacity for anionic surfactants. Subsequently the optimal production method was used for the other combinations: MgFe and ZnAl-LDHs. Since LDH stability is essential for long time use it was investigated for different circumstances during an extended period of time.

To produce high concentration (HC) LDH a solution of 86 gram $Mg(NO_3)_2 \cdot 6H_2O$ and 64 gram $Al(NO_3)_3 \cdot 9H_2O$ in 100 ml Milli-Q water was added to a second solution of 18.6 gram NaOH and 11 gram Na_2CO_3 in 100 ml Milli-Q water. To produce low concentration (LC) LDH a solution of 43 gram $Mg(NO_3)_2 \cdot 6H_2O$ and 32 gram $Al(NO_3)_3 \cdot 9H_2O$ in 100 ml Milli-Q water was added to a second solution of 18.6 gram NaOH and 11 gram Na_2CO_3 in 100 ml Milli-Q water.

Both solutions were pumped at a rate of 10 ml/min in a beaker and mixed with a magnetic stirrer. During dosing the precipitation starts immediately. At the end of the dosing the precipitate formed was allowed to age overnight at 60 °C under continues stirring. The aged precipitate was filtered with a Buchner funnel and washed 10 times with each time 100 ml of fresh Milli-Q water in a centrifuge. The final product was dried overnight at 105 °C and calcined at 450 °C for 4.5 hours (Reichle 1986).

2.3 Storage

The materials were stored in five different atmospheres: in an exicator with silica and flushed with N_2 (dry N_2: no water vapour and CO_2 present), in an exicator with silica not flushed with N_2 (dry air: no water vapour, but CO_2 present), in a closed vial, in open air and stored in water.

2.4 Characterization

The samples were characterized by powder X-ray diffraction (XRD), thermo gravimetric analysis (TGA) and scanning electron microscope (SEM). X-ray diffraction patterns of the powdered samples were obtained using a PANalytical APD with CuKα radiatior (50 kV and 35 mA) at a scanning rate of 1.5°/min. Thermo gravimetric analysis were carried out using a Setaram Setsys 16. The temperature programmed rate was 1 °C/min, and the weight change was measured from 20 to 800 °C. The nitrogen gas flow was 49 ml/min. The morphology was observed using a Jeol Scanning Electron Microscope JSM-6480LV.

The specific surface area, pore size and pore volume distribution were measured using the Micromiretics Tristar 3000. The samples are pre-treated overnight to remove water and other contaminants from the pores. During the

Table 1 Characteristics of the produced LDHs. PLDH is precipitated LDH, ALDH is aged LDH, CLDH is calcined LDH (Fig. 1)

Sample	Cations M^{2+} and M^{3+}	Ratio M^{2+}/M^{3+} [–]	Measured ratio [–]	Amount of mmol M^{3+}/g	BET surface area [m²/g]	Pore volume [cm³/g] at $p/p_0 = 0.99$	$d(003)$ [nm]	a [nm]	c [nm]
CLDH	Mg^{2+} Al^{3+}	2	2.1	4.8	169	0.47			
CLDH	Mg^{2+} Al^{3+a}	2	1.9	5.0	164	0.37			
CLDH	Mg^{2+} Al^{3+}	1.5	1.0	7.4	193	0.57			
CLDH	Mg^{2+} Al^{3+}	2	1.7	4.8	183	0.58			
CLDH	Mg^{2+} Al^{3+}	3	2.9	3.7	65	0.29			
PLDH	Mg^{2+} Al^{3+}				0.02	0	0.741	0.304	2.22
ALDH	Mg^{2+} Al^{3+}				69	0.23	0.735	0.303	2.21
CLDH	Mg^{2+} Al^{3+}	2	2.1	3.6	188	0.62			
PLDH	Mg^{2+} Al^{3+}				1.6	0	0.736	0.310	2.21
ALDH	Mg^{2+} Al^{3+}				72	0.21	0.740	0.310	2.22
CLDH	Mg^{2+} Fe^{3+}	2	1.9	5.3	87	0.34			
CLDH	Zn^{2+} Al^{3+}	2	5.5	1.9	31	0.15			

[a]This LDH is produced with high concentration (HC) initial solutions; all other LDHs are produced with low concentration (LC) initial solution

pre-treatment, a nitrogen flow is applied and the samples are heated to 105 °C. The amount of cations in the samples was measured by ICP (Perkin Elmer 5300 DV).

2.5 Adsorption experiments

The adsorption experiments were conducted at different initial surfactant concentrations ranging from 0.5 to 1 g/kg water. Surfactants are dissolved in milli-Q water. An amount of 0.1 gram LDH and 80 ml surfactant solution were mixed in a screw capped flask and placed in a shaking bath (Julabo SW22) for 48 hours (to ensure equilibrium) at 25 °C. The initial solution is pH neutral. After equilibration the pH is measured again. The water phase was sampled with a syringe equipped with a filter to remove suspended solids (Spartan 30/0.45RC (0.45 μm)) and the surfactant concentration was measured. The concentration of LAS was determined by spectrophotometry at 223 nm (Shimadzu UV-1650PC) (accuracy correlation curve: 2%).

3 Results and discussion

3.1 Characterization

Table 1 summarizes the measured characteristics of the produced LDH samples. In most cases the expected M^{2+}/M^{3+} ratio is confirmed by the measured ratio. The Mg^{2+}/Al^{3+} ratio 1.5 is actually 1 and Zn^{2+}/Al^{3+} ratio 2 is measured 5.5. From this point onwards these measured ratios will be

used. The amount of M^{3+} per gram of CLDH is calculated. At M^{2+}/M^{3+} ratio 2, there is approximately 5 mmol M^{3+}/g CLDH present. The BET surface area of PLDH is increased after aging (ALDH) and increased further after calcination (CLDH). The surface area of MgAl-CLDH is in the range 160–200 m²/g. This is higher than the surface area of 120 m²/g described by Reichle (1986). The difference can be explained by calcination; the samples of Reichle are not calcined. During calcination the CO_3^{2-} molecules are converted to CO_2. CO_2 eludes and leaves a porous structure behind and thus a higher surface area. Increasing the M^{2+}/M^{3+} ratio to 3 decreases the surface area and pore volume substantially. LDH with the other cations also gave a substantial decrease of surface area and pore volume.

The XRD measurements of the powdered MgAl and MgFe-LDHs with M^{2+}/M^{3+} ratio 2 are shown in Figs. 2 and 3. The three samples shown in these figures are samples taken during synthesis as indicated in Fig. 1: at point 3 after precipitation and before aging (PLDH), at point 6 after aging (ALDH) and at point 7, after calcination (CLDH).

The XRD patterns for PLDH and ALDH samples show well defined (00l) reflections at lower 2θ values and clear (110) reflections at higher 2θ values, indicating a typical LDH pattern for both MgAl and MgFe. The reflections are indexed to a hexagonal lattice with rhombohedral 3R symmetry (Zou et al. 2006). The lattice parameters are calculated accordingly and presented in Table 1. The sharp peak at $d = 0.74$ nm ($2\theta = 12°$) is ascribed to the diffraction by

Fig. 2 XRD patterns of MgAl-LDH: samples taken before aging (*PLDH*), after aging (*ALDH*) and after calcination (*CLDH*) (M^{2+}/M^{3+} ratio 2; LC initial solutions)
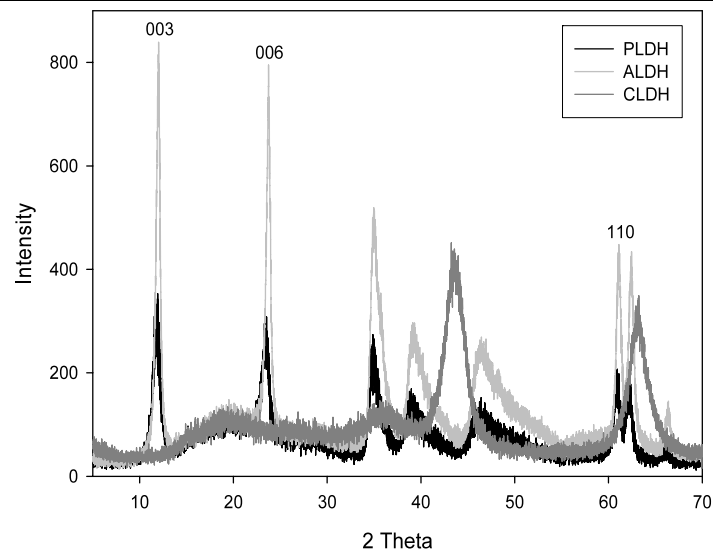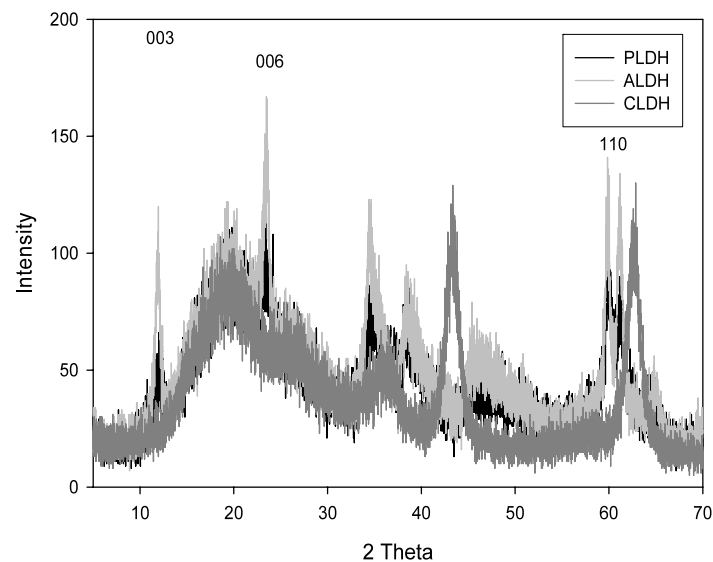

Fig. 3 XRD patterns of MgFe-LDH: samples taken before aging (*PLDH*), after aging (*ALDH*) and after calcination (*CLDH*) (M^{2+}/M^{3+} ratio 2; LC initial solutions)

planes (003) and is referred to as the basal spacing. From the width of the brucite-like layers (0.48 nm), the interlayer space is calculated and is 0.26 nm. This indicates a carbonate anion located between the layers. Lattice parameter *a* corresponds to the average closest metal-metal distance within a layer and is calculated as twice the position of the $d(110)$ ($2\theta = 60°$) (Trujillano et al. 2006). The parameter *c* is a function of the average charge of the metal cations, the nature of interlayer anion and the water content. The values for $d(003)$, *a* and *c* shown in Table 1 are in agreement with those reported in the literature for LDHs (Zou et al. 2006; Trujillano et al. 2006).

The intensity of the reflection is much higher and accordingly the line width is smaller for MgAl (Fig. 2) compared to MgFe-LDH (Fig. 3). This corresponds to a higher crystallinity of MgAl-LDH (Kloprogge et al. 2004). This can also be concluded for the aged samples (ALDH) compared

to the not aged samples (PLDH). During aging the crystallinity increases, as expected.

For the calcined samples (CLDH) the absence of the (003) reflection peak indicate the destruction of the layered structure by calcination. The samples show a similar pattern to the one of magnesium oxide, as expected and described in literature (Reichle 1986; Cavani et al. 1991; Tao et al. 2006).

Figure 4 shows the TGA for MgAl-ALDH with a M^{2+}/M^{3+} ratio of 2. A three-stage degradation mechanism can be identified in this figure. The first weight loss up to 190 °C is due to the removal of physisorbed and interlayer water molecules. The second stage up to 380 °C is due to the conversion of hydroxyl groups of the brucite-like layers into oxide groups. The third stage up to 620 °C is due to the decomposition of the interlayer carbonate anion (Anbarasan et al. 2005). The formed carbondioxide will elude from the

Fig. 4 TGA analysis of MgAl-ALDH (M^{2+}/M^{3+} ratio 2; LC initial solutions)
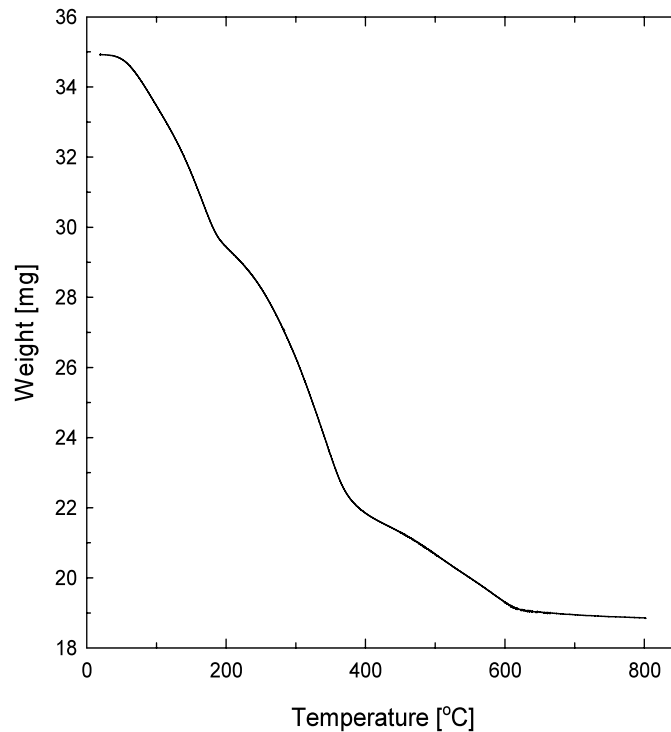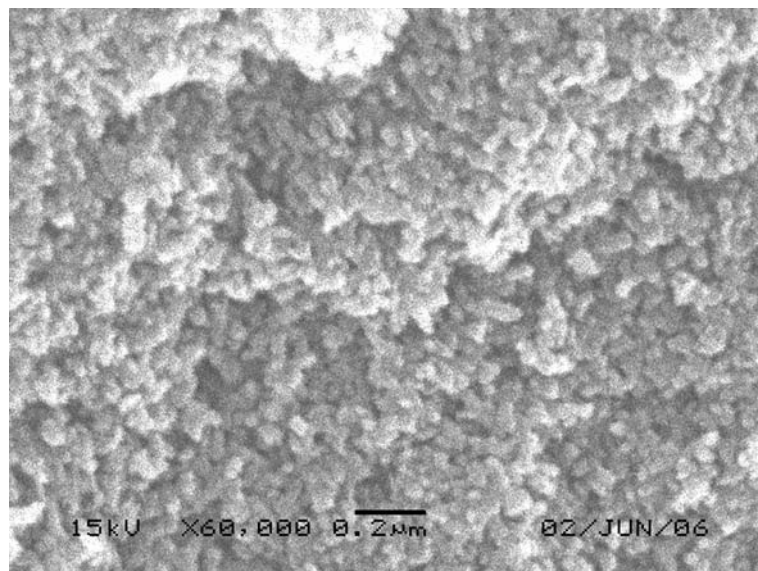
Fig. 5 SEM pictures of MgAl-ALDH (M^{2+}/M^{3+} ratio 2; LC initial solutions)

LDH and a porous structure will stay behind (Ulibarri et al. 1995). This is a typical TGA for LDH (Frost et al. 2005).

A SEM picture of MgAl ALDH with a M^{2+}/M^{3+} ratio of 2 is shown in Fig. 5. The picture shows an aggregate that consists of crystallites with a size of tens of nanometres (Xu et al. 2005). In between the nanoparticles (crystallites) a porous network exists. The size of the pores in this network is in same order of magnitude, namely between 10 and 80 nm (not shown, measured by Tristar).

3.2 Adsorption experiments

Increasing the crystallinity could increase the stability (Xu et al. 2005). The crystallinity can be increased by decreasing the concentration of the initial solutions; therefore the initial concentration of the magnesium nitrate and aluminium nitrate solution is varied. The high concentration (HC) solution was taken at the saturation point of aluminium nitrate and the low concentration (LC) was at 50% of that saturation point. The amount of magnesium nitrate was fixed because

Table 2 BET surface area and pore volume of fresh CLDH samples and after storage. y = years, m = months

Cations M^{2+} and M^{3+}	Ratio M^{2+}/M^{3+} [–]	Concentration of initial solutions	Storage method	Time of storage	BET surface area [m^3/g]	Pore volume [cm^3/g] at $p/p_0 = 0.99$
Mg^{2+} Al^{3+}	2	LC	–	0	169	0.47
Mg^{2+} Al^{3+}	2	LC	dry N$_2$	4 m	149	0.50
Mg^{2+} Al^{3+}	2	LC	dry air	4 m	154	0.48
Mg^{2+} Al^{3+}	2	LC	vial	4 m	116	0.43
Mg^{2+} Al^{3+}	2	LC	air	4 m	77	0.39
Mg^{2+} Al^{3+}	2	LC	water	4 m	58	0.29
Mg^{2+} Al^{3+}	2	HC	–	0	164	0.37
Mg^{2+} Al^{3+}	2	HC	dry N$_2$	4 m	104	0.25
Mg^{2+} Al^{3+}	2	HC	dry air	4 m	85	0.25
Mg^{2+} Al^{3+}	2	HC	vial	4 m	132	0.33
Mg^{2+} Al^{3+}	2	HC	air	4 m	42	0.17
Mg^{2+} Al^{3+}	2	HC	water	4 m	66	0.26
Mg^{2+} Al^{3+}	1	LC	–	0	193	0.57
Mg^{2+} Al^{3+}	1	LC	vial	1.5 y	95	0.30
Mg^{2+} Al^{3+}	1	LC	water	2.3 m[a]	100	0.43
Mg^{2+} Al^{3+}	2	LC	–	0	183	0.58
Mg^{2+} Al^{3+}	2	LC	vial	1.5 y	33	0.13
Mg^{2+} Al^{3+}	2	LC	water	2.3 m[a]	97	0.35
Mg^{2+} Al^{3+}	3	LC	–	0	65	0.29
Mg^{2+} Al^{3+}	3	LC	vial	1.5 y	13	0.07
Mg^{2+} Al^{3+}	3	LC	water	2.3 m[a]	12	0.03
Mg^{2+} Al^{3+}	2	LC	–	0	188	0.62
Mg^{2+} Al^{3+}	2	LC	water	2.5 m	60	0.24
Zn^{2+} Al^{3+}	5.5	LC	–	0	31	0.15
Zn^{2+} Al^{3+}	5.5	LC	vial	1 y	41	0.15
Zn^{2+} Al^{3+}	5.5	LC	water	2.3 m[a]	37	0.14
Mg^{2+} Fe^{3+}	2	LC	–	0	87	0.34
Mg^{2+} Fe^{3+}	2	LC	water	2.5 m	26	0.06

[a]After storage in a vial (time: see line above), subsequently stored in water

of the fixed M^{2+}/M^{3+} ratio. The difference in adsorption capacity between the fresh CLDHs prepared with high concentration (HC) and low concentration (LC) appeared not significant (not shown). The HC and LC-CLDH samples are both stored at different conditions; dry N$_2$, dry air, in a vial, in open air and in water. During storage, samples were taken in time and the adsorption capacity, specific surface area and pore volume were measured. The specific surface areas and pore volumes are shown in Table 2. The adsorption capacities for LC-CLDH stored in dry N$_2$ and in water are shown in Fig. 6.

The surface area and pore volume of LC-CLDH stored in dry N$_2$ decreased slightly (Table 2). The largest decrease in surface area and pore volume was found after storage in water. The presence of water vapour (closed vial and open air) also induces a decrease in surface area and pore volume. The presence of CO$_2$ (in dry air) does not have any effect. The decrease in adsorption capacity was related to the storage method in the same way as the surface area and pore volume. Storage in dry N$_2$ had no effect on adsorption capacity. The fluctuation of the adsorption capacity is within the error limits. Whereas storage in water decreased adsorption capacity to about 30% of its initial adsorption capacity

Fig. 6 LAS adsorption capacity in time of MgAl-CLDH stored in dry N_2 and in water (M^{2+}/M^{3+} ratio 2; LC initial solutions). Experiments are carried out with 80 ml initial solution (0.5 gLAS/kg water) and 0.1 gram of CLDH
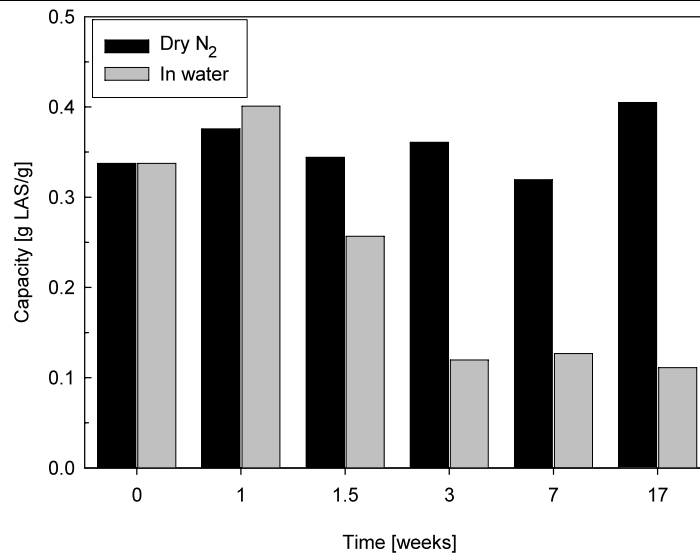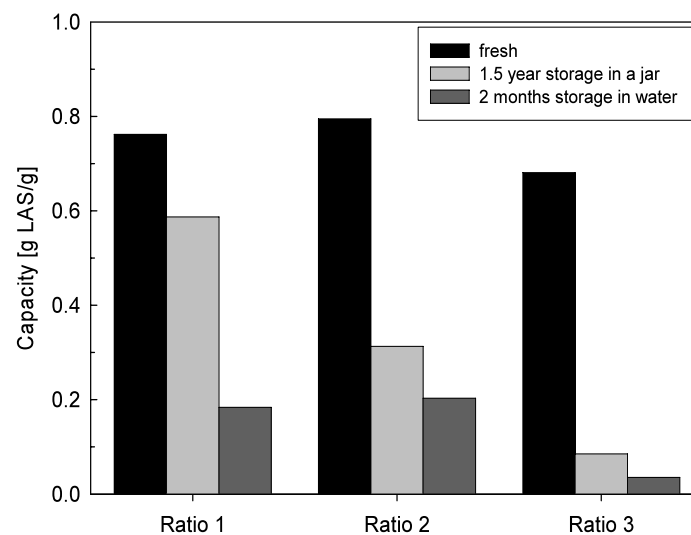

Fig. 7 LAS adsorption capacity of CLDH with different Mg/Al ratios (LC initial solutions); fresh, after 1.5 year storage in a jar and after 2 months of storage in water. Experiments are carried out with 80 ml initial LAS solution (1 gLAS/kg water) and 0.1 gram of CLDH

(Fig. 6). In all the adsorption experiments the pH increased, due to the exchange of OH^- ions for LAS molecules. The pH increases with increasing adsorption capacity.

CLDH is hydrophilic and will adsorb water from the air. When CLDH is stored in water, the interconnection between the crystallites is more easily destroyed. After drying, the crystallites form denser aggregates. This decreases the surface area and pore volume and accordingly the adsorption capacity. Furthermore, Al^{3+} is leaching from the brucite-like structure into the water. The amount of Al^{3+} leached to the storage water for HC-CLDH is higher (0.18 mmol/gLDH) compared to LC-CLDH (0.02 mmol/gLDH). This is explained by a higher crystallinity for LC-CLDH. Therefore, CLDHs in this study are further produced with low concentration initial solutions.

Figure 7 represents the LAS adsorption capacity for MgAl-CLDH prepared with ratios 1, 2 and 3. The LAS ad-

sorption capacity obtained for MgAl ratio 1 and 2 are higher compared to ratio 3. The lower ratio indicates more Al^{3+} cations and by that a higher charge density which should lead to a higher LAS adsorption capacity. MgAl ratio 1 did not result in a higher adsorption capacity compared to ratio 2; this can be caused by the production of other metal oxides next to LDH (Reichle 1986). Based on the measured adsorption capacity for fresh CLDH, the ratio 2 seems to be optimal and was selected for further experiments. This optimum ratio is comparable to Zhao and Nagy (2004) for the adsorption of sodium dodecyl sulphate onto MgAl-CLDH.

After synthesis the materials have been stored in a vial for 1.5 year. Subsequently the materials were stored in water for two months. After both storage conditions the LAS adsorption capacity, specific surface area and pore volume were measured. The results are presented in Fig. 7 and Table 2.

Fig. 8 LAS adsorption capacity of MgAl, MgFe and ZnAl-CLDH (Mg^{2+}/Al^{3+} or Fe^{3+} ratio 2; Zn^{2+}/Al^{3+} ratio 5.5; LC initial solutions). Results are given for samples just after preparation (fresh) and after 2 months of storage in a water. ZnAl-CLDH was stored beforehand in a vial for 1 year. Experiments are carried out with 80 ml initial solution (1 gLAS/kg water) and 0.1 gram of CLDH
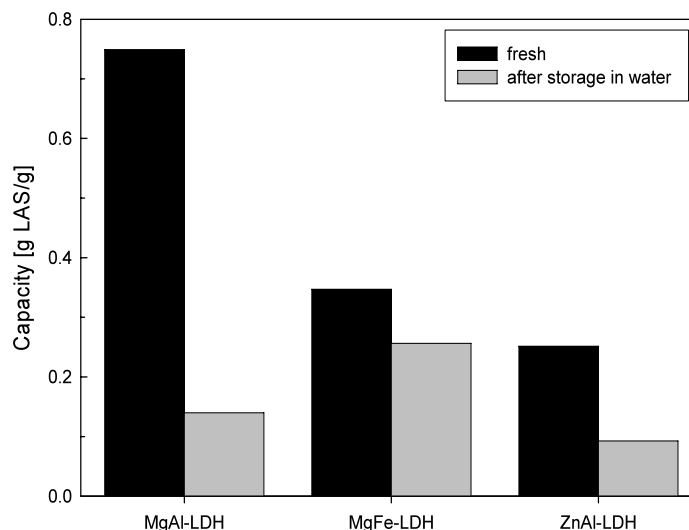
After 1.5 year of storage, the adsorption capacity reduced dramatically for ratios 2 and 3 but only a small reduction was observed for ratio 1. Subsequently storing the samples in water for 2 months induced a further reduction of the adsorption capacity of all three CLDH samples (Fig. 7). The specific surface area and pore volume show a decrease after storing in a vial for 1.5 year (Table 2). This can be explained by the rearrangement of the nano sized crystallites of the LDH aggregates. The crystallites form aggregates through interconnection at the edges of different crystallites and the glue effect of amorphous LDH materials (Xu et al. 2005). In time the crystallites can slip past each other and form a denser structure, which explains the decrease in surface area, pore volume and thereby the reduction in adsorption capacity. A further reduction of adsorption capacity after storing in water can be caused by leaching of Al^{3+} from the brucite-like structure.

The last process parameter that was investigated is the type of cations. Four cations were used to produce CLDH: Mg^{2+}, Zn^{2+} and Al^{3+}, Fe^{3+}. Three sets of cations with ratio 2 were used to prepare CLDH starting from an initial solution with a low concentration: MgAl, MgFe and ZnAl-CLDH. The LAS adsorption capacity, specific surface area and pore volume were measured after synthesis and after storage. The results are presented in Fig. 8 and Table 2. MgAl and MgFe-CLDH were stored in water for two months and ZnAl-CLDH was stored in a vial for one year and subsequently stored in water for two months.

The adsorption capacity directly after preparation is much higher for MgAl-CLDH compared to MgFe and ZnAl-CLDH (Fig. 8). This is in agreement with the higher specific surface area and pore volume of MgAl-CLDH as shown in Table 2. The XRD measurements of MgAl-LDH and MgFe-LDH already showed a large difference in intensity, which indicates a difference in crystallinity (Figs. 2

and 3). During MgFe-LDH synthesis only a small amount of MgFe-LDH is formed next to iron oxides (Fe_2O_3) and magnesium oxides (MgO), which explains the lower adsorption capacity. The lower adsorption capacity for ZnAl-CLDH is explained by the lower charge density, because of the lower M^{2+}/M^{3+} ratio (5.5 instead of 2).

The adsorption capacity of the CLDHs after storage in water is reduced mainly for MgAl and ZnAl. The measured adsorption capacity for MgFe-CLDH is mainly the adsorption capacity of Fe_2O_3 and MgO and they seem to be more stable in aqueous surroundings. Therefore, these oxides could be of interest as alternative water stable low cost detergent adsorbents.

4 Conclusions

In this work the process parameters of the co-precipitation method to produce LDH and their effect on the LDH structure, stability and adsorption capacity for LAS are investigated. The BET surface area of precipitated LDH (PLDH) is increased after aging (ALDH) and increased further after calcination (CLDH). During calcination the CO_3^{2-} molecules are converted to CO_2, which leaves a porous structure behind. XRD measurements show an increase in crystallinity after aging and a destruction of the layered structure after calcination. The highest adsorption capacity is obtained for CLDH with a M^{2+}/M^{3+} ratio of 1 and 2 because of the highest charge density compared to ratio 3. Storing the CLDH samples in water resulted in a reduction of adsorption capacity and a decrease in surface area and pore volume. This is caused by the rearrangement of the nano size crystallites of which a LDH aggregate exist. The crystallites slip past each other and form a denser structure. The crystallinity can be improved by using low concentration initial solutions; this decreases the leaching of M^{3+}

from the brucite-like structure into the water. The ideal storage method is in a dry N_2 atmosphere. The highest LAS adsorption capacity was obtained for MgAl-CLHD, where the production process was not optimal for ZnAl and MgFe-CLDH. The application of CLDH in a small device to reuse laundry rinsing water is not promising for long term use. CLDH is instable and the adsorption capacity of anionic surfactants reduces dramatically in aqueous surroundings.

References

Adak, A., Bandyopadhyay, M., Pal, A.: Removal of anionic surfactant from wastewater by alumina: a case study. Colloid Surf. A Physicochem. Eng. Aspects **254**(13), 165–171 (2005)

Anbarasan, R., Lee, W.D., Im, S.S.: Adsorption and intercalation of anionic surfactants onto LDH, a XRD study. Bull. Mater. Sci. **28**(2), 145–149 (2005)

Cavani, F., Trifiro, F., Vaccari, A.: Hydrotalcite-type anionic clays: preparation, properties and applications. Catal. Today **11**, 173–301 (1991)

Frost, R.L., Martens, W.N., Erickson, K.L.: Thermal decomposition of the hydrotalcite: Thermogravimetric analysis and hot stage Raman spectroscopic study. J. Therm. Anal. Calorim. **82**(3), 603 (2005)

Holmberg, K., Jonsson, B., Kronberg, B., Lindman, B.: Surfactants and Polymers in Aqueous Solution, pp. 357–387. Wiley, Chichester (2003)

Kloprogge, J.T., Hickey, L., Frost, R.L.: The effects of synthesis pH and hydrothermal treatment on the formation of zinc aluminum hydrotalcites. J. Solid State Chem. **177**(11), 4047–4057 (2004)

Kopka, H., Beneke, K., Lagaly, G.: Anionic surfactants between double metal hydroxide layers. J. Colloid Interface Sci. **123**(2), 427–436 (1988)

Lazaridis, N.K., Asouhidou, D.D.: Kinetics of sorptive removal of chromium(VI) from aqueous solution by calcined MgAlCO3 hydrotalcite. Water Res. **37**, 2875–2882 (2003)

Lazaridis, N.K., Matis, K.A., Webb, M.: Flotation of metal-loaded clay anion exchangers. Part I: the case of chromates. Chemosphere **47**, 373–378 (2001)

Lazaridis, N.K., Hourzemanoglou, A., Matis, K.A.: Flotation of metal-loaded clay anion exchangers. Part II: the case of arsenates. Chemosphere **47**, 319–324 (2002)

Pavan, P.C., Gomes, G.A., Valim, J.B.: Adsorption of sodium dodecyl sulphate on layered double hydroxides. Microporous Mesoporous Mater. **21**, 659–665 (1998)

Pavan, P.C., Crepaldi, E.L., Gomes, G.D., Valim, J.B.: Adsorption of sodium dodecylsulfate on a hydrotalcite-like compound. Effect of temperature, pH and ionic strength. Colloid Surf. A Physicochem. Eng. Aspects **154**, 399–410 (1999)

Pavan, P.C., Crepaldi, E.L., Valim, J.B.: Sorption of anionic surfactants on LDH. J. Colloid Interface Sci. **229**, 346–352 (2000)

Pavlovic, I., Barriga, C., Ulibarri, M.A., Hermosin, M.C., Cornejo, J.: Adsorption of acidic pesticides 2,4-D, Clopyralid and Picloram on calcined hydrotalcite. Appl. Clay Sci. **30**(2), 125–133 (2005)

Pringadi, P.: Sud Chemie Germany, Ostenrieder Str. 15, 85368 Moosburg, Germany. Personal communication, July 2005

Ramakrishnan, V.: Unilever Research India, 64 Main Road, Whitefield P.O. Bangalore 560066, India. Personal communication, December 2004

Reichle, W.T.: Synthesis of anionic clay minerals. Solid State Ionics **22**, 135–141 (1986)

Reis, M.J., Silverio, F., Tronto, J., Valim, J.B.: Effect of pH, temperature, and ionic strength on adsorption of sodium dodecylbenzenesulfonate into Mg-Al-CO3 layered double hydroxides. J. Phys. Chem. Solids **65**, 487–492 (2004)

Schouten, N., van der Ham, A.G.J., Euverink, G.J., de Haan, A.B.: Selection and evaluation of adsorbents for the removal of anionic surfactants from laundry rinsing water. Water Res. **41**, 4233–4241 (2007)

Shin, H.S., Kim, M.J., Nam, S.Y., Moon, H.C.: Phosphorus removal by hydrotalcite-like compounds. Water Sci. Technol. **34**(1–2), 161–168 (1996)

Tao, Q., Zhang, Y., Zhang, X., Yuan, P., He, H.: Synthesis and characterization of layered double hydroxides with a high aspect ratio. J. Solid State Chem. **179**(3), 708–715 (2006)

Trujillano, R., Holgado, M.J., Pigazo, F., Rives, V.: Preparation, physicochemical characterisation and magnetic properties of Cu-Al layered double hydroxides with CO32- and anionic surfactants with different alkyl chains in the interlayer. Phys. B **373**(2), 267–273 (2006)

Ulibarri, M.A., Pavlovic, I., Hermosin, M.C., Cornejo, J.: Hydrotalcite like compounds as potential sorbents of phenols from water. Appl. Clay Sci. **10**, 131–145 (1995)

Xu, Z.P., Stevenson, G.S., Lu, C.Q., Lu, G.Q., Bartlett, P.F., Gray, P.P.: Stable suspension of layered double hydroxide nanoparticles in aqueous solution. J. Am. Chem. Soc. **128**(1), 36–37 (2005)

Zhao, H., Nagy, K.L.: Dodeyl sulfate-hydrotalcite nanocomposites for trapping chlorinated organic pollutants in water. J. Colloid Interface Sci. **274**, 613–624 (2004)

Zhu, M.X., Li, Y.P., Xie, M., Xin, H.Z.: Sorption of an anionic dye by uncalcined and calcined LDH. J. Hazard. Mater. **120**(1–3), 163–171 (2005)

Zou, K., Zhang, H., Duan, X.: Studies on the formation of 5-aminosalicylate intercalated Zn-Al layered double hydroxides as a function of Zn/Al molar ratios and synthesis routes. Chem. Eng. Sci. **62**(7), 2022–2031 (2006)