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Adsorption of fatty acids to layered double hydroxides in aqueous systems

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Abstract Due to their anion exchange characteristics, layered double hydroxides (LDHs) are suitable for the detoxification of aqueous, fatty acid containing fermentation substrates. The aim of this study is to examine the adsorption mechanism, using crude glycerol from plant oil esterification as a model system. Changes in the intercalation structure in relation to the amount of fatty acids adsorbed are monitored by X-ray diffraction and infra-red spectroscopy. Additionally, calcination of LDH is investigated in order to increase the binding capacity for fatty acids. Our data propose that, at ambient temperature, fatty acids can be bound to the hydrotalcite by adsorption or in addition by intercalation, depending on fatty acid concentration. The adsorption of fatty acids from crude glycerol shows a BET-like behavior. Above a fatty acid concentration of 3.5 g L^{-1}, intercalation of fatty acids can be shown by the appearance of an increased interlayer spacing. This observation suggests a two phase adsorption process. Calcination of LDHs allows increasing the binding capacity for fatty acids by more than six times, mainly by reduction of structural CO_3^{2-}.

Keywords Fatty acids · Hydrotalcite · Layered double hydroxides · Adsorption · Glycerol

1 Introduction

Layered double hydroxides (LDHs), also called hydrotalcite-like materials, are known as anion exchanging clays. They are made up of layers containing metal cations, leading to an overall positive charge. The charge is neutralized by intercalation of exchangeable anions (Auerbach et al. 2004). Structurally, hydrotalcite is derived from the mineral brucite ($Mg(OH)_2$), in which some of the Mg^{2+} cations in the layer structure were replaced by Al^{3+} in octahedral sites. The Mg^{2+} ions are coordinated six-fold to hydroxyl groups. Electroneutrality is maintained by carbonate ions intercalated between the layers. The chemical formula of hydrotalcite is $Mg_{0.75}Al_{0.25}(OH)_2(CO_3)_{0.5}\text{-}0.5H_2O$ (Bergaya et al. 2006). The thickness of the interlayer between the Al^{3+} and Mg^{2+} containing sheets is dependent on the number, size, and strength of the bonds between the anions and hydroxyl groups (Cavani et al. 1991). LDHs are used for a wide variety of applications in catalysis and polymer, pharmaceutical and medical industries. Some of the classical applications of LDHs are listed in the following. Because of the wide variety of its chemical compositions and large specific surface area, LDHs are common in the field of catalysis. Reactions catalyzed by LDHs are, for example, Michael addition, Aldol condensation, Claisen-Schmidt, Knoevenagel and Henry reactions (Cavani et al. 1991; Evans and Duan 2006). Their low toxicity, buffering effect, and exchange capacity make LDHs very useful for pharmaceutical, medical, and cosmetic applications. In medicine they are used as antacids or delivery systems for pharmaceuticals (Auerbach et al. 2004).

The main commercial application of LDH is that of an additive for polymers. Here they are used as thermal stabilizers or flame retardants because of their ability to

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neutralize large amounts of acids, that are generated during heating or degradation of poly(vinyl chloride) (Auerbach et al. 2004). Additionally, LDHs have been reported to be used in the field of water treatment, as adsorbents, as ion exchangers, and in other applications. They can take up a variety of toxic substances from the environment through anion-exchange, reconstruction, and adsorption. Sorbents described in this context are 2,4,6-trinitrophenol, dodecyl benzenesulfonate, phosphate, and toxic inorganic anions such as SeO_3^{2-}, SeO_4^{2-}, and $Cr_2O_7^{2-}$. Furthermore, removal of metal cations from aqueous solutions and adsorption of carbon dioxide are described (Bergaya et al. 2006). Intercalation reactions are of particular interest, as they can be used to change the chemical, electronic, optical, and magnetic properties of a host lattice. In addition, intercalation reactions, as a low temperature method, can lead to novel materials, which may not be accessible via other techniques (Khan and ÓHare 2002).

For the intercalation of mono- and dicarboxylic aliphatic acids into LDH, five different mechanisms are summarized by Carlino (Carlino 1997). Carboxylic acids can be intercalated by the direct ion exchange method, whereat the LDH is shaken in a suitably concentrated solution of the desired carboxylic acid or its salt (Borja and Dutta 1992). The co-precipitation method requires the addition of an M^{II}/M^{III} salt solution to a base solution containing the carboxylic acid as the anion. This solution is then crystallized using the same method as for the preparation of the LDH host material (Reichle 1986). The rehydration method is similar to the direct ion exchange method, with the difference that water-free calcined LDH is used. The LDHs can be slowly heated up in a mixture with a suitable organic acid to the melting point of the acid. The mixture is held at this temperature for about 8 h before slowly cooling down again (Carlino and Hudson 1994). The glycerol effected exchange requires the LDH to be stirred with a glycerol containing solution of the desired carboxylic acid or its salt, whereas the glycerol leads to a swelling of the interlayer space. This swelling alleviates the intercalation of the carboxylic acids (Hansen 1991).

Borja et al. describe the packing of fatty acids intercalated in LDHs. They show that dependent on the charge distribution of the LDH, the carboxylic acids form either a monomolecular or a bimolecular film. In the case of $Mg_3Al\text{-}LDH^+$ a bimolecular film is formed. They reason that there must be two different incorporation mechanisms: simple ion-exchange introduces $RCOO^-$ and forms single layers, intercalation of RCOOH leads to the formation of bilayers. According to Borja et al. this depends mainly on the chain length of the adsorbate (Borja and Dutta 1992).

Free fatty acids have been found to be present in crude glycerol in concentrations up to 6 % (w/w). Furthermore fatty acids are known to inhibit the growth of microorganisms like *Clostridium butyricum* and *Clostridium diolis*. These organisms can be used to convert crude glycerol to 1,3-propanediol. For a fermentative utilization of crude glycerol a pretreatment to remove the fatty acids may be necessary. In a previous study we have studied the adsorption of free fatty acids from crude glycerol and could show that this had a beneficial effect on the subsequent fermentation (Chatzifragkou et al. 2010; Wiesen et al. 2014). In this study, the mechanism of the adsorption process will be discussed.

For the quantification of fatty acids in aqueous solutions there are two well established methods available. On the one hand, there is the gravimetric determination of non-volatile lipophilic substances after solvent extraction according to DIN 38409-56. Alternatively, in some systems it is also possible to determine the acid content via titration. Both methods do not give information about the fatty acid composition. For measuring the fatty acid content in organic systems, derivatization and subsequent analysis via gas chromatography is a common method. In aqueous systems, gas chromatographic analysis of fatty acids is possible after extraction of the free fatty acids in a suitable solvent prior to derivatization. The extractant has to provide an almost quantitative extraction efficiency and an adequate chemical environment for the derivatization reaction.

The model system we worked with is crude glycerol, which is a side product from the transesterification of plant oils in the biodiesel production. The adsorption process was examined with X-ray diffraction and infra-red spectroscopy. Additionally calcination of the hydrotalcite was analyzed as a method to improve the binding properties for fatty acids (Bergaya et al. 2006).

2 Materials and methods

2.1 Materials

The Hydrotalcite powder used in this study was supplied by the Clariant-Produkte (Deutschland) GmbH (Moosburg, Germany). The crude glycerol that we utilized in this study was prepared by PPM Magdeburg as described in the following. The plant oil was partially refined, which means degummed and neutralized. 20 kg of partially refined high oleic rapeseed oil was heated up to 60 °C. After reaching the temperature, a sodium methoxide solution containing 100 g of sodium methoxide and 1.28 kg of methanol was added. The mixture was stirred at 60 °C for 4 h and then settled down over night. The fatty acid methyl ester phase was then separated from the aqueous glycerol phase and washed with distilled water at 50 °C until pH 7 was reached. Afterwards, the methyl ester was dried at 60 °C under vacuum until the liquid was clear. The rapeseed oil used for the transesterification contained 78 % oleic acid, 11.4 % linoleic acid, and 3.3 % palmitic acid. The crude glycerol was diluted with deionized water and the pH was set to 8 as an agreement between the low stability of MgAl hydrotalcite in an acidic environment and a positive surface charge of the material (Basu et al. 2014). Crude glycerol solutions contain, although of aqueous nature, free fatty acids in concentrations of up to 20 g L^{-1}, which is illustrated in Fig. 2. The fatty acids form an emulsion, which is stable for several months, in the water-glycerol-methanol mixture.

2.2 Analytics

For the extraction of fatty acids from the aqueous solutions ethyl acetate was used. The extraction was performed with a phase relationship of 1:1 for 30 s on a vortex. After that, 100 μL of the organic phase were derivatized using 50 μL of a 0.25 M TMSH-solution (trimethylsulfonium hydroxide) in methanol. The sample was analyzed using a Clarus 560 gas chromatograph as previously described (Wiesen et al. 2014). X-ray powder diffraction patterns were obtained with a Siemens D5005 X-ray powder diffractometer using Cu Kα radiation. Infrared spectra were collected on a Perkin Elmer 100FT-IR spectrometer. The particle surface charge was measured with a BTG Mütek PCD-03 particle charge detector.

2.3 Adsorption of fatty acids from crude glycerol

The adsorbent used in the adsorption experiments was obtained by heating the material EXM 2152 in a Heraeus M1100/2 muffle furnace at 500 °C for 3 h. The adsorption was carried out in 15 mL polyethylene tubes with a volume of 10 mL of the corresponding crude glycerol solution and 0.2 g of the adsorbent. The suspension was mixed with an overhead shaker at room temperature for 8 h, respectively for the designated time in the kinetic experiments. The concentrations were measured with GC after solvent extraction with ethyl acetate.

3 Results and discussions

3.1 Characterization of the adsorbent

In the following, the hydrotalcite adsorbent is referred to as EXM 2152. The corresponding XRD pattern is shown in Fig. 1. The material is identified as hydrotalcite (syn) due to its basal reflections. A d-value of 0.76 nm can be calculated from the 2θ values of the main reflections. The BET surface is determined with 11.5 m^2 g^{-1}.

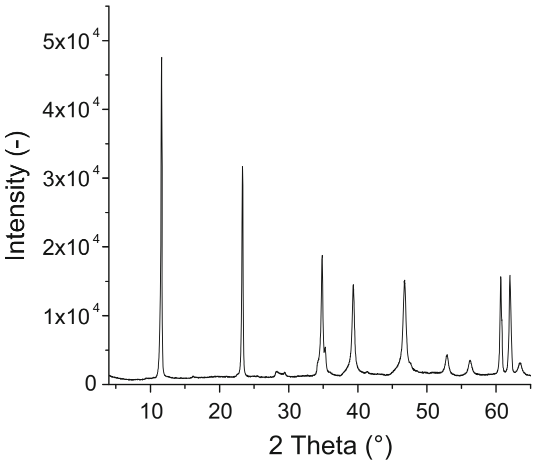

Fig. 1 Powder X-ray diffractogram of hydrotalcite EXM 2152

3.2 Model system crude glycerol

For the isotherm adsorption experiments, differently concentrated aqueous solutions of fatty acids have been prepared, in order to investigate the characteristics of the fatty acids in the model system crude glycerol. Therefore a stock solution of 200 g L^{-1} of crude glycerol in H_2O_{dest}, adjusted to a pH of 8, was further diluted, resulting in different concentrations of fatty acids. The fatty acid concentration as a function of the crude glycerol concentration can be seen in Fig. 2. For crude glycerol concentrations of up to 50 g L^{-1}, a linear relationship between crude glycerol concentration and fatty acid content can be determined. With rising crude glycerol concentrations the fatty acid content flattens, due to the low solubility of the organic acids in the aqueous system, which leads to the precipitation of small amounts of the organic acids. It is noticeable

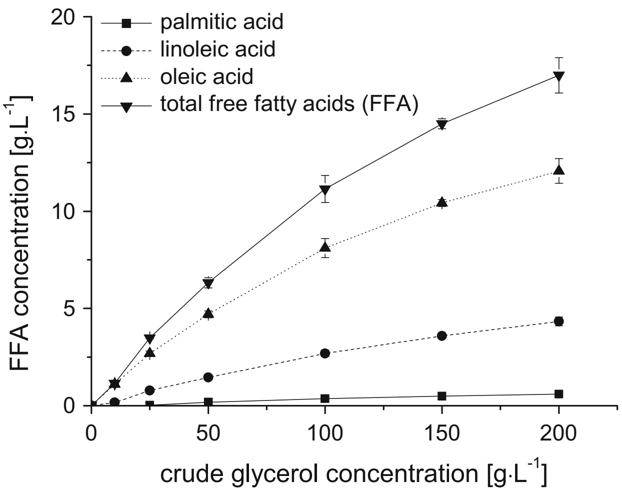

Fig. 2 Free fatty acid (FFA) content at different concentrations of crude glycerol (CG) in aqueous solution at a pH of 8

that the fatty acid concentration in the crude glycerol solution is much higher than the solubility in water, which is below 0.05 g L^{-1}. Fatty acids can be found in a stabilized emulsion in the system, which is apparent in the cloudiness of the crude glycerol solutions. The figures for the total amount of fatty acids are calculated by summing up the amounts of oleic acid, linoleic acid and palmitic acid.

3.3 Calcination

The structural effects of calcination to hydrotalcites are widely described in literature and have been summarized by Bergaya (Bergaya et al. 2006). Around 250 °C the LDHs are losing their interlayer water. With mid-infrared (MIR) spectroscopy measurements the following observations could be made. The carbonate ν_3 band (1360 cm^{-1}) starts to split into two bands at 1330 and 1540 cm^{-1}. This is probably due to grafting of carbonate ions to the hydroxide layers. Additionally, the formation of tetrahedral coordinated Al can be observed at temperatures up to 500 °C. From 250 to 500 °C, the layer structure collapses and the LDH converts to a mixed-oxide MgO-like phase. At around 900 °C, the mixed oxide decomposes to MgO and $MgAl_2O_4$ spinel (Bergaya et al. 2006). The splitting of the carbonate band and the disappearing of the resulting bands can be observed in Fig. 3a with rising calcination temperatures. This shows that the material is steadily losing carbonate anions during calcination. At 700 °C almost no carbonate band is detectable. The same can be observed with the interlayer water, represented by the peak at about 3400 cm^{-1}. There are a few more changes in the region of wavenumber 650–1000 cm^{-1}. Changes in these regions represent alterations in the lattice structure (Kameda et al. 2006), but these differences are not significant enough for interpretation. Figure 3b shows the loadings for fatty acids depending on the previously applied calcination temperature. It can be seen that the capacity for fatty acids rises with increasing calcination temperature. Rising the calcination temperature from 300 to 400 °C leads to a 5.7-fold increased loading for fatty acids. A further elevation of the temperature results in a minor, but consistent capacity augmentation up to 700 °C. The reduced content of structural CO_3^{2-}, which is hardly exchanged, leads to a higher anion exchange capacity with increasing calcination temperature (Châtelet and Bottero 1996). Additionally, the heat treatment removes the interlayer water, which could also favor an increased fatty acids adsorption. The following experiments have been performed with EXM 2152, calcined at 500 °C.

3.4 Adsorption kinetics

For the adsorption studies, the concentration of the total amount of fatty acids is considered. The time course for the equilibrium of fatty acid adsorption onto EXM 2152 is shown in Fig. 4a. The equilibrium is attained within 2 h. To describe the adsorption process, two well established models were applied: the kinetic model of pseudo-first order which can be seen in Eqs. 1 (Lagergren 1898) and 2 (linearized form) and the model for pseudo-second order kinetics as shown in Eqs. 3 and 4 (Ho and McKay 1999).

$$q_t = q_{eq} * \left(1 - e^{-k*t}\right) \tag{1}$$

$$\ln\left(q_{eq} - q_t\right) = lnq_{eq} - k_1 t \tag{2}$$

$$q_t = k_2 t\left(q_{eq} - q_t\right) q_{eq} \tag{3}$$

$$t/_{q_t} = 1/\left(k_2 q_{eq}^2\right) + t/q_{eq} \tag{4}$$

where q_{eq} and q_t [mg g^{-1}] are the adsorption quantities for the hydrotalcite at equilibrium and time t, k [h^{-1}] is the first order rate constant, k_2 is the second order rate constant [g mg^{-1} min^{-1}] and t [h] is the adsorption time. To examine the applicability of the models, they need to be fitted to the experimental data. This is done in the linearized form and the results are plotted in Fig. 4b. Both models differ considerably in regard to the regression coefficient of the linear fit. The pseudo-second order model

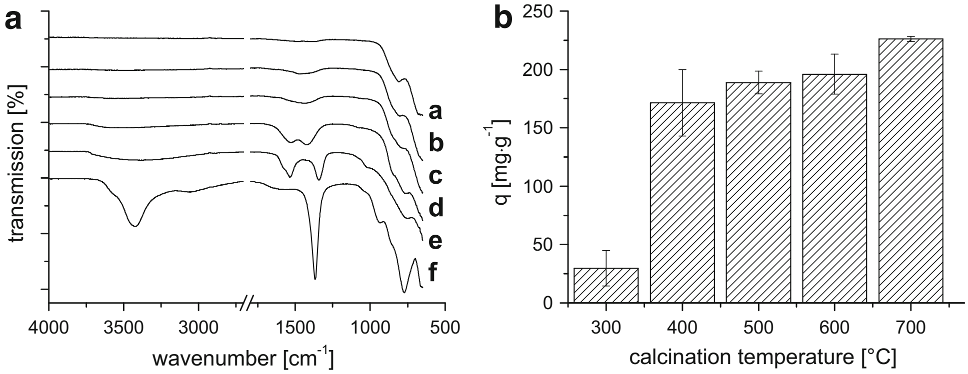

Fig. 3 Influence of rising calcination temperatures on the MIR-spectrum (**a**) (*a* 700 °C, *b* 600 °C, *c* 500 °C, *d* 400 °C, *e* 300 °C and *f* untreated) and the binding capacity for fatty acids (**b**) of the hydrotalcite EXM 2152. The calcination temperature was hold for 3 h

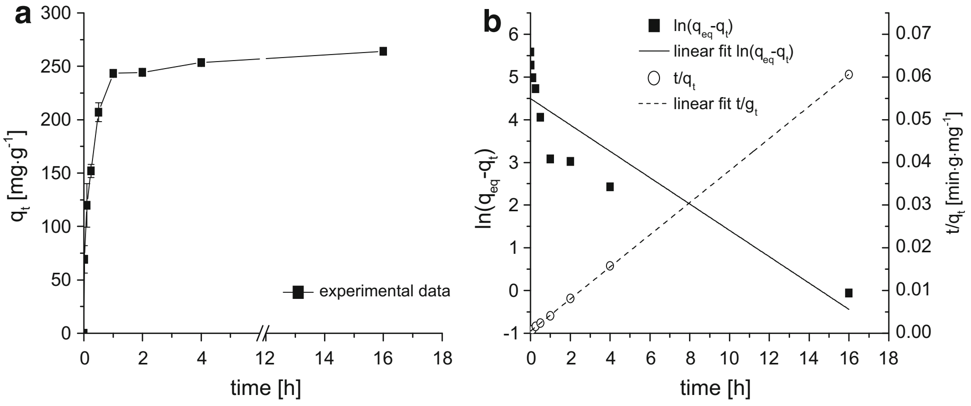

Fig. 4 **a** Adsorption kinetics of EXM 2152 for fatty acids. **b** Linearized plots for the pseudo-first and pseudo-second order kinetics of the adsorption

shows a R^2 value of 0.999, whereas the fit of the Lagergren equation results in a R^2 value of 0.773. In addition to the low regression coefficient, the intercept of the linear fit leads to an irresolute value for q_{eq} of 89.5 mg g^{-1}. From the slope of the second order kinetics, a value of 265.9 mg g^{-1} can be determined for q_{eq}, which corresponds to the loadings that can be seen in Fig. 4a. Furthermore, a value of 0.0279 g mg^{-1} min^{-1} can be calculated from the intercept of the second order kinetics for k_2. According to Ho, a kinetic of second order shows that the rate of adsorption determines the overall kinetics, whereas transport processes within the adsorbent are of minor importance (Ho and McKay 1999).

3.5 Adsorption isotherm

The shape of the isotherm in Fig. 5 looks like the type IV isotherm from the Brunauer classification (Brunauer and Deming 1940). Usually, these types of isotherms can be observed with a formation of a second surface layer of adsorbate, either on a plane surface or on the wall of a pore (Ruthven 1984). The formation of multiple layers of fatty acids on a surface was also observed for steel by Lundgren et al. (Lundgren et al. 2007). So the shape of the isotherm can be interpreted as evidence for multilayer adsorption, especially regarding the roughly twofold increase of the loading from about 230 to almost 400 mg g^{-1} after the flat intercept between 6 and 12 g L^{-1} of fatty acids. The adsorption mechanism was additionally examined by XRD-analysis after adsorption, to see an influence on the basal spacing.

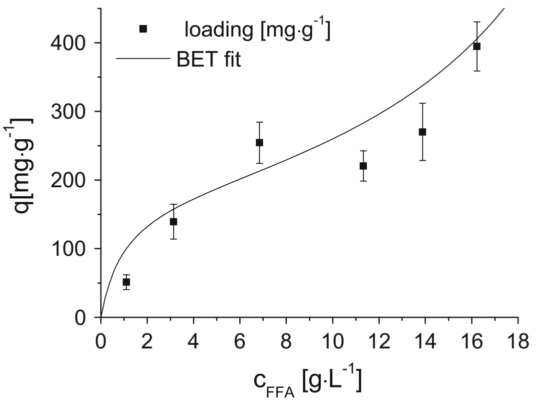

Fig. 5 Adsorption isotherm of EXM 2152 with fatty acids from crude glycerol. The data are fitted with Brunauer–Emmett–Teller Model with a R^2 value of 0.87

The presence of fatty acid anions on EXM 2152 after the treatment of crude glycerol (Fig. 6a) is confirmed by the characteristic CH_2 stretching vibrations between 2920 and 2851 cm^{-1} as well as by vibration bands at 1451 and 1412 cm^{-1}. The latter are corresponding to asymmetric and symmetric stretching vibrations of the COO^- groups, as can be seen in Fig. 6a. In the hydrotalcites loaded with a crude glycerol concentration higher than 25 g L^{-1} (Fig. 6b), several bands can be observed in the ν_{sym} (CO) stretching region at 1563 and 1538 cm^{-1}. At a crude glycerol concentration of 50 g L^{-1}, this is a single peak at 1538 cm^{-1} that converts into a peak at 1563 cm^{-1} with a shoulder at 1538 cm^{-1}. This phenomenon has been described by Xu et al., who have observed this kind of change in IR spectra when the amount of the organic anions in the exchange solution is close to the anion exchange capacity. They reasoned that this is a result of an interpenetrating packing mode (Xu and Braterman 2010). With crude glycerol concentrations of 100 g L^{-1} and higher, there are additional shoulders for both peaks, this being an evidence for a bilayer packing (Borja and Dutta 1992). These results show that the intercalation structure is not only dependent on the host mineral and the guest molecule, but also on the adsorbent concentration during the adsorption phase. Carlino et al. propose a “flat stack” formation, where the carboxylate anions are packed parallel to the layers for low adsorbate concentrations (Carlino 1997). The big peaks at 1638 cm^{-1} in Fig. 6b represent remaining interlayer carbonate anions. A strong peak at a

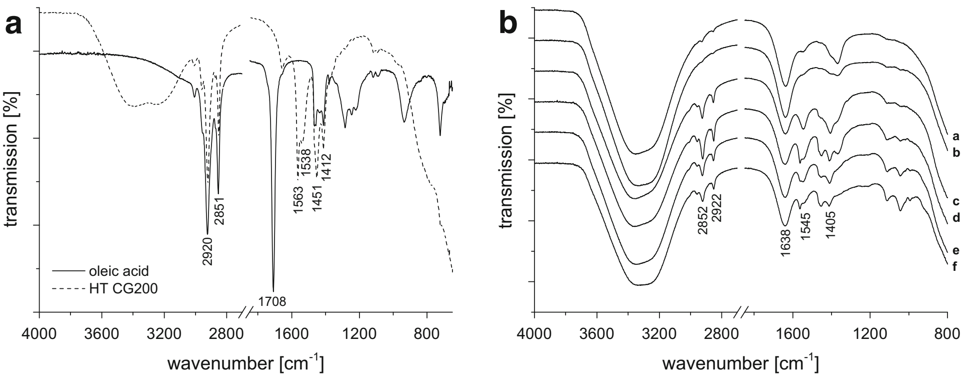

Fig. 6 **a** Comparison of pure oleic acid and hydrotalcite, calcined at 500 °C, incubated with CG 50. **b** ATR spectra of EXM 2152, calcinated at 500 °C, loaded with differently concentrated crude glycerol (CG) solutions. *a* CG 10, *b* CG 25, *c* CG 50, *d* CG 100, *e* CG 150, and *f* CG 200 (g L^{-1})

frequency from 1725 to 1700 cm^{-1} is characteristic for a carboxylic group, that can be seen in Fig. 6a (Coates 2000).

Figure 7 shows the X-ray diffractograms of three samples of calcined EXM 2152 that have been treated with 25, 50 and 200 g L^{-1} of crude glycerol. These three concentrations of crude glycerol represent different characteristic parts of the isotherm as shown in Fig. 5. The figure shows that after adsorption from a 25 g L^{-1} concentrated crude glycerol solution, the basal reflection (003) corresponds to an interlayer spacing of 0.76 nm, which is the same as found with the untreated hydrotalcite (Fig. 1). Treatment with 50 and 200 g L^{-1} of crude glycerol leads to a shift of the basal reflection (003). The resulting interlayer spacing is 3.44 nm, whereas the CG 50 sample still shows a reflection at $2\theta = 11.336°$. This indicates the presence of some hydrotalcite without fatty acids intercalated between the layers. These results confirm that at low fatty acid concentrations the adsorption mechanism differs from the intercalation process, which occurs at fatty acid concentrations above 6 g L^{-1}, as shown in Fig. 5. The large d-spacing of 3.44 nm also points to the formation of a bilayer structure (Borja and Dutta 1992; Meyn et al. 1993). Since the d-spacing after adsorption with 25 g L^{-1} crude glycerol is equal to the d-spacing in the unloaded material, the “flat stack” formation has not been confirmed in our experiments.

3.6 pH-dependence of fatty acid adsorption

Figure 8 shows the binding capacities of EXM 2152 for fatty acids within a pH range from pH 3 to pH 11. The adsorption is the lowest at a pH of 11 and rises with falling of the pH to pH 5. At a pH of 3 the adsorption is lower again, which could be linked to the low stability of the hydrotalcites at low pH levels (Ookubo et al. 1993). Another explanation for the decreased adsorption at pH 3 is the behavior of free fatty acids at different pH values. At a low pH, they start to precipitate and to build another liquid phase. Hereby, the fatty acid concentration in the aqueous phase gets lower and so does the loading of the hydrotalcite. The adsorption shows a strong correlation with the zeta potential of the hydrotalcite (referred to as Syntal 696)

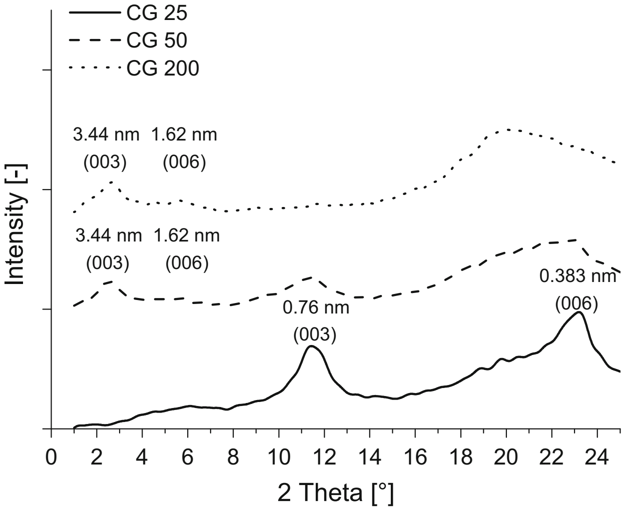

Fig. 7 X-ray diffractograms of EXM 2152 after loading with 25, 50 and 200 g L^{-1} of crude glycerol (CG)

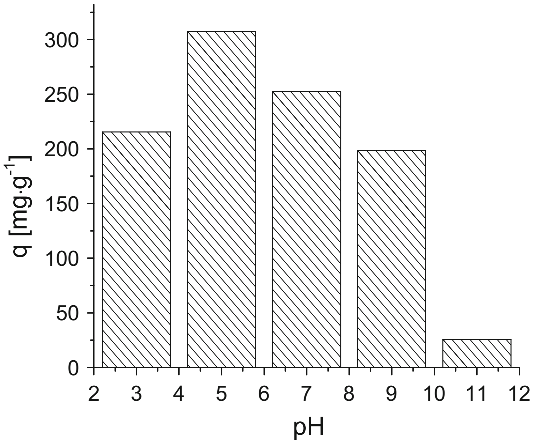

Fig. 8 pH-dependent loading of EXM 2152 with fatty acids from crude glycerol

which is described by Ralla et al. (Ralla et al. 2011). The material exhibits a positive potential of almost 40 mV at a pH of 6 that slowly decreases to about 22 mV at pH 10 and further down to −20 mV at a pH of 12. The isoelectric point can be found around pH 10. The binding behavior of the synthetic hydrotalcite follows the behavior of an anion exchanger, which indicates, that there are electrostatic interactions between fatty acids and adsorbent. With a surrounding pH between 5 and 9, the material has a positively charged surface and can act as an anion exchanger. When the surface potential becomes neutral or negative, the capacity sinks to a low level. Without a positive surface potential, almost no adsorption can be monitored, whereas hydrophobic effects are described to be crucial for the interpenetration packing mode (Xu and Braterman 2010). This examination gives strong evidence that the primary binding mechanism is that of anionic exchange.

4 Conclusions

This work has focused on the application of hydrotalcite for the adsorption of fatty acids. This kind of adsorption can be useful to purify fermentation broths, biodiesel, oil mill wastewater, etc. For these processes, novel insights into the binding mechanism are given. By application of a synthetic hydrotalcite, fatty acids can be adsorbed from an aqueous crude glycerol solution. The adsorption kinetic can be described with the pseudo-second order model, resulting a q_e of 265.9 mg g^{-1} and a k_2 of 0.0279 g mg^{-1} min^{-1}. Several observations demonstrate that the adsorption mechanism takes place in different phases. The BET-like isotherm shows that after an initial adsorption, which is probably due to ion exchange at the adsorbent surface, a second adsorption phase occurs. The XRD data exhibit a remarkable increase of the d-spacing, raising the crude glycerol concentration from 25 to 100 g L^{-1}. Within this concentration range, a transition takes place that leads to intercalation of fatty acids in between the brucite sheets. No further variation of the d-spacing could be monitored. The pH dependent capacities confirm that the initial adsorption is based on ion exchange.

Calcination of the hydrotalcite leads to a gain in the loading capacity by factor 7.5. This is the result of several factors: on the one hand, interlayer water and CO_3^{2-} are expelled during the heating, on the other hand, structural parameters like pore size and surface area are increased. Another adsorption experiment has shown a similar capacity for fatty acids, when solubilizing them in oleic acid methyl ester (OAME) (data not shown). Glycerol is known to affect the ion exchange by penetrating the interlayer and bringing it to swell. This reduces the strength of the hydrogen bonding that exists between the carbonate anion and hydroxide layers. This lowers the carbonatés resistance to getting replaced by a different anion. This swelling effect can also be caused by alcohols (Auerbach et al. 2004). The glycerol-effected exchange is not responsible for the adsorption in OAME. The adsorption from the glycerol solution could be affected by this effect. Researching the mechanism of intercalation can, on the one hand, be helpful to improve adsorption processes using hydrotalcites as adsorbents and, in addition, can help to generate functionalized hydrotalcites for further applications.

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References

Auerbach, S.M., Carrado, K.A., Dutta, P.K.: Handbook of Layered Materials. CRC Press, Boca Raton (2004)

Basu, D., Das, A., Stöckelhuber, K.W., Wagenknecht, U., Heinrich, G.: Advances in layered double hydroxide (LDH)-based elastomer composites. Prog. Polym. Sci. **39**, 594–626 (2014)

Bergaya, F., Theng, B.K.G., Lagaly, G.: Handbook of Clay Science. Elsevier, Amsterdam (2006)

Borja, M., Dutta, P.: Fatty acids in layered metal hydroxides: membrane-like structure and dynamics. J. Phys. Chem. **5444**, 5434–5444 (1992)

Brunauer, S., Deming, L.S., Deming, W.E., Teller, E.: On a theory of the van der Waals adsorption of gases. J. Am. Chem. Soc. **62**(7), 1723–1732 (1940). doi: 10.1021/ja01864a025

Carlino, S.: The intercalation of carboxylic acids into layered double hydroxides: a critical evaluation and review of the different methods. Solid State Ion. **98**, 73–84 (1997)

Carlino, S., Hudson, M.: Reaction of molten sebacic acid with a layered (Mg/Al) double hydroxide. J. Mater. Chem. **4**, 99–104 (1994)

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

Châtelet, L., Bottero, J.: Competition between monovalent and divalent anions for calcined and uncalcined hydrotalcite: anion exchange and adsorption sites. Colloids Surf. **111**, 167–175 (1996)

Chatzifragkou, A., Dietz, D., Komaitis, M., Zeng, A.-P., Papanikolaou, S.: Effect of biodiesel-derived waste glycerol impurities on biomass and 1,3-propanediol production of *Clostridium butyricum* VPI 1718. Biotechnol. Bioeng. **107**, 76–84 (2010)

Coates, J.: Interpretation of infrared spectra, a practical approach interpretation of infrared spectra, a practical approach. In: Meyers, R.A. (ed.) Encyclopedia of Analytical Chemistry, pp. 10815–10837. Wiley, Hoboken (2000)

Evans, D.G., Duan, X.: Preparation of layered double hydroxides and their applications as additives in polymers, as precursors to magnetic materials and in biology and medicine. Chem. Commun. (Camb). **5**, 485–496 (2006)

Hansen, H.C.B.: The use of glycerol intercalates in the exchange of CO_3^{2-} with SO_4^{2-}, NO_3^{-}OR Cl^{-} in pyroaurite-type compounds. Clay Miner. **26**, 311–327 (1991)

Ho, Y.S., McKay, G.: Pseudo-second order model for sorption processes. Process Biochem. **34**, 451–465 (1999)

Kameda, T., Saito, M., Umetsu, Y.: Preparation and characterisation of Mg–Al layered double hydroxides intercalated with 2-naphtalene sulphonate and 2,6-naphtalene disulphonate. Mater. Trans. **47**, 923–930 (2006)

Khan, A.I., ÓHare, D.: Intercalation chemistry of layered double hydroxides: recent developments and applications. J. Mater. Chem. **12**, 3191–3198 (2002)

Lagergren, S.: Zur Theorie der sogenannten Adsorption gelöster Stoffe. K. Sven. Vetenskapsakademiens. Handl. **24**, 1–39 (1898)

Lundgren, S.M., Persson, K., Mueller, G., Kronberg, B., Clarke, J., Chtaib, M., Claesson, P.M.: Unsaturated fatty acids in alkane solution: adsorption to steel surfaces. Langmuir **23**, 10598–10602 (2007)

Meyn, M., Beneke, K., Lagaly, G., Chemie, A., Kiel, U.: Anion-exchange reactions of hydroxy double salts. Inorg. Chem. **32**(7), 1209–1215 (1993)

Ookubo, A., Ooi, K., Hayashi, H.: Preparation and phosphate ion-exchange properties of a hydrotalcite-like compound. Langmuir **9**, 1418–1422 (1993)

Ralla, K., Sohling, U., Suck, K., Sander, F., Kasper, C., Ruf, F., Scheper, T.: Adsorption and separation of proteins by a synthetic hydrotalcite. Colloids Surf. B Biointerfaces. **87**, 217–225 (2011)

Reichle, W.: Synthesis of anionic clay minerals (mixed metal hydroxides, hydrotalcite). Solid State Ion. **22**, 135–141 (1986)

Ruthven, D.M.: Principles of Adsorption and Adsorption Processes. Wiley, Frederictown (1984)

Wiesen, S., Tippkötter, N., Muffler, K., Suck, K., Sohling, U., Ruf, N., Ulber, R.: Adsorptive vorbehandlung von rohglycerin für die 1,3-propandiol fermentation mit *Clostridium diolis*. Chemie Ing. Tech. **86**, 129–135 (2014)

Xu, Z.P., Braterman, P.S.: Synthesis, structure and morphology of organic layered double hydroxide (LDH) hybrids: comparison between aliphatic anions and their oxygenated analogs. Appl. Clay Sci. **48**, 235–242 (2010)