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LAYERED DOUBLE HYDROXIDES AS ACTIVE ENVIRONMENTAL CLEANERS OF POLLUTED WATER

BY

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Abstract. Environmental problems are more prevalent nowadays and one of the big concerns is water contamination by highly toxic pollutants. The employment of adsorption technologies constitutes a powerful tool for the reduction of water pollution because of the mild conditions required by adsorption and its good efficiency in pollutant removal processes. Defined by a versatile micro/nanotexture layered double hydroxides (LDH) can be fabricated to own specific nanoarchitectonics hence, they are proposed nowadays as efficient adsorbents. This work presents MgAlLDH and the derived calcined forms to be employed as efficient adsorbents to treat aqueous mediums polluted with industrial dyes (*e.g.*: Nylosan Navy). Results reveal a strong connection between the adsorption efficiency and the micro/nanomorphology features of the LDH. The structure and morphology properties of the LDHs were studied by XRD, FESEM and N_2 adsorption techniques. These findings might pave the way to establish novel solutions to remove toxic compounds from aqueous mediums by using LDHs as efficient environmental cleaners in water technologies.

Keywords: LDH, pollutant, nano/micromorphology, adsorption.

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1. Introduction

Increasing interests regarding engineered nanomaterials with specific nano/microarchitecture have generated a strong need to define their behaviours and impacts as efficient environmental cleaners in water technologies. Hydrotalcite-like anionic clays (LDH) belong to the class of 2-D layered materials and are represented by the general formula: $[M^{II}_{1-x}M^{III}_{x}(OH)_{2}]^{x+}[Am^{-x/m}\cdot nH_{2}O]^{x-}$. They are built up of sheets of edge – sharing metal octahedra where, by comparison of brucite $M(OH)_2$, part of Mg^{2+} is replaced by Al^{3+} cations; the excess of the positive charge is counterbalanced by exchangeable anions A^{m-}, located as water molecules, in the interlayer spaces (Carja *et al.*, 2005). The incorporation of cations with redox properties in the LDH network or the intercalation of a large variety of anions in the interlayer space offer the opportunity to obtain efficient adsorbent materials with a unique combination of acid - base properties, a large surface area and a tuneable micro/nanotexture. Nowadays the design and fabrication of LDH materials with tailored nano or micro architectonics is a subject of increasing interest (Hibino, 2018).

Colours from dyes brighten our world and are used majorly in industries such as the paper, plastic, leather, and textile. By the year 2017, the annual global dyestuff production was estimated to be around 37 million tons, out of which 14% goes out as effluents from various industries hence, these dyes are a matter of serious concern to environmental, specific water pollution. Synthetic dyes, that are soluble in water, are highly toxic causing negative effects on all life forms because of their composition thus, they can cause important health issues on account of their toxic nature (Hailu *et al.*, 2017). Therefore, it is highly desirable to remove the industrial dyes from aqueous environment before its recycle and reuse. Several methods were reported for removal of dyes. Among them, adsorption is the most effective and low cost technique for removal of dye molecule in the condition of designing and use of some innovative materials/biomaterials (Lazaridis and Asouhidou, 2003). Recent research have formulated cost efficient adsorbents based on LDH matrices (Zubair *et al.*, 2017; Mittal, 2021). It was recently reported that LDHs with Mg^{2+} and Al^{3+} as the constituent cations, a combination that is among the most frequently studied, clearly show high adsorption features that can be tailored as a function of their micro/nanomorphology.

In this context, this work presents the adsorption of an industrial dye, namely Nylosan Navy (NN), using as novel adsorbents 2-D LDH matrices containing Mg^{2+} and Al^{3+} as cations of the anionic clay layers and by considering the characteristics of micro/nanomorphology of MgAlLDH. Furthermore, we tested the adsorption characteristics of the mixed oxides that formed, as a result of MgAlLDH calcination at 550°C and 850°C, respectively. NN is an industrial dye that was kindly offered by Clariant Produkte, Switzerland and used as received.

2. Experimental

Materials and characterization techniques

Synthesis of the LDH was carried out by coprecipitation, following the coprecipitation method (Mishra *et al.*, 2018), in which 100 mL of an aqueous solution of $Mg(NO_3)_2 \cdot 6H_2O$ (0.03 M)/ $Al(NO_3)_3 \cdot 9H_2O$ (0.01M) and aqueous solution of the precipitants NaOH Na_2CO_3 were added dropwise together, in such a way that the pH remained at a constant value of 9.5. The resulting white precipitate was aged at 338 K for 24 h under stirring separated by centrifugation, washed extensively with warm deionized water until sodium free and then dried under vacuum at 338 K. This sample was denoted as MgAlLDH, while after the calcination at 550°C and 850°C, for 8 hours, the samples were denoted as LDH550 and LDH850, respectively.

XRD: X-ray powder diffraction patterns were recorded on a Philips PW 1840 diffractometer using monochromatic CuK_λ radiation (λ = 0.154 nm), operating at 40 kV and 30 mA over a 2θ range from 4 to 70 degree.

N_2 adsorption at 77 K: N_2 adsorption isotherms were measured on a Coulter SA 3100 automated gas adsorption system. Prior to the measurements the samples were heated under vacuum at 383 K, for 5 h, in order to expel the interlayer water molecules. Microcomputer processing controlled the analysis. The BET specific surface area (SBET) was calculated by using the standard Brunauer, Emmett and Teller method on the basis of the adsorption data (Sing, 1985). The texture of the sample was also studied by a Mira II LMU Tescan field-emission scanning electron microscopy (FESEM). Surface area of the samples was determined from nitrogen adsorption–desorption isotherms at liquid nitrogen temperature using a Coulter SA 3100 instrument with 8 h lasting outgas at 110°C.

Adsorption experiments

Adsorption experiments were made by a batch technique at room temperature. The batch mode was selected because of its simplicity and reliability. Known amounts of MgAlLDH were placed in different Erlenmeyer glass flasks of 100 ml capacity containing 40 mL of NN solution of known concentration and pH (Zubair, 2017). The solutions were shaken vigorously for a given time period to reach equilibrium. The stirring speed was 500 rot/min for each run. After an established contact time t (min), the sample were withdrawn from the shaker, the suspensions were centrifuged at 5000 rpm for 10 min and the supernatant was centrifuged for 10 min. The concentration of the NN in the aqueous solution was analysed by the UV spectrophotometer. The concentration of NN was calculated by the difference of initial concentration, C_0, and the concentration at time t C_t, as Q_e(mg/g), by the equation 1:

$$Q_e = C_0 - C_t / m \times 1/V \tag{1}$$

where C_0 is the initial concentration of the dye in the initial solution (mg/L), C_t is the concentration of the dye in solution at a given time t (mg/L), V is the total volume of the solution (mL); and m is the mass of the adsorbent (g). At the adsorption equilibrium, the dye concentration in the feed C_t becomes the equilibrium concentration C_e and adsorbed amount Q_t is equal to Q_e.

Adsorption experiments, for studying the effect of solution pH, were conducted as follows: 0.1 g of MgAlLDH was suspended in 25 mL of NN aqueous solutions. The pH of the solution was adjusted in the range 4–12 by adding dilute solution of HCl or sodium hydroxide (0.5 M NaOH or 0.5 M HCl), the agitation time was fixed to 2 h and the temperature was the room temperature °C.

3. Results and discussion

Figure 1 displays the powder XRD patterns of MgAlLDH, but also thermal treated LDH550 and LDH850. For the brucite-like MgAlLDH the diffraction peaks are typical to the LDH's structure (Carja *et al.*, 2005) with sharp and symmetric reflections of the basal (003), (006) and (009) planes and broad, less intense, asymmetric reflections for the nonbasal (012), (015) and (018) planes as shown in Fig. 1.

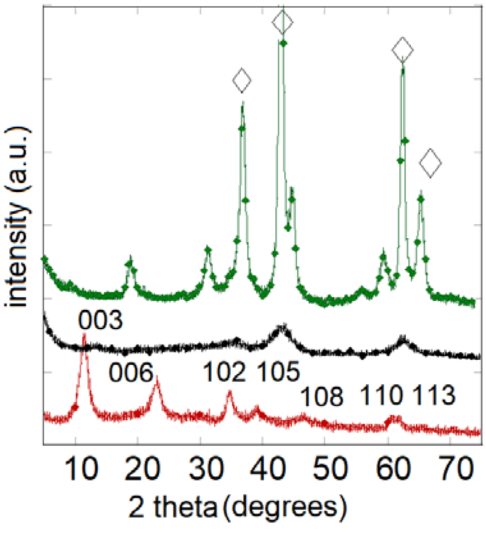

Fig. 1 – The XRD patterns of (🟥) MgAlLDH, (⬛) LDH550 (🟩) LDH850.

The XRD reflections were indexed using a hexagonal cell with rhombohedral symmetry (R – 3m), commonly used as a description of the LDH structure. The parameter a, calculated as 2×d(110), is a function of the metal - metal distance within the layers, pointing out the cations stacking in the 003 planes, while the c parameter, calculated as 3×d(003) (Bouberka *et al.*, 2005), is a function of the average charge of the metal cations, the nature of the interlayer anions and the water content of the hydrotalcite - like sample. The value of the lattice parameter a is equal to 3.059 Å for all MgAlLDH samples. The decrease in the c parameter can be attributed to the modified electrostatic interactions between the layer and the interlayer network when the synthesis temperature was modified (Gilea and Carja, 2017). After calcination at 550°C (see Fig. 1) the hydrotalcite structure completely collapsed and the new reflections indicate the presence, in LDH550, of poorly crystallized mixed oxides that are characteristic to the LDH calcined at this temperature (Miyata and Okada, 1977). The XRD pattern of the samples, calcined at 850°C, gives information about the evolution of the newly formed mixed oxides. For LDH850 the corresponding XRD pattern (see Fig. 1) shows strong peaks that are characteristic to a well crystalized phase of (◊) $MgAl_2O_4$, pointing out that the formation of this structure.

The SEM image of MgAlLDH is presented in Fig. 2a. At first glance the micrograph would indicate a high crystalline material formed by enough uniform particles, that are up to 1µm in size; however, a closer look points out that these particles consist of overlapped, highly agglomerated nanoparticles, irregular in sizes and/or shape and showing an average diameter equal to 110 nm. The SEM results, of the LDH calcined at 550°C or 850°C, are enough similar so in Figure 2b we presented the SEM image of LDH850. It reveals the presence of the LDHs platelets with chopped edges and an average size of about 120 mm and 90 nm for LDH550 and LDH850, respectively. This is simply because of the changes in structure from the LDHs to the mixtures of the mixed oxides, due to the calcination.

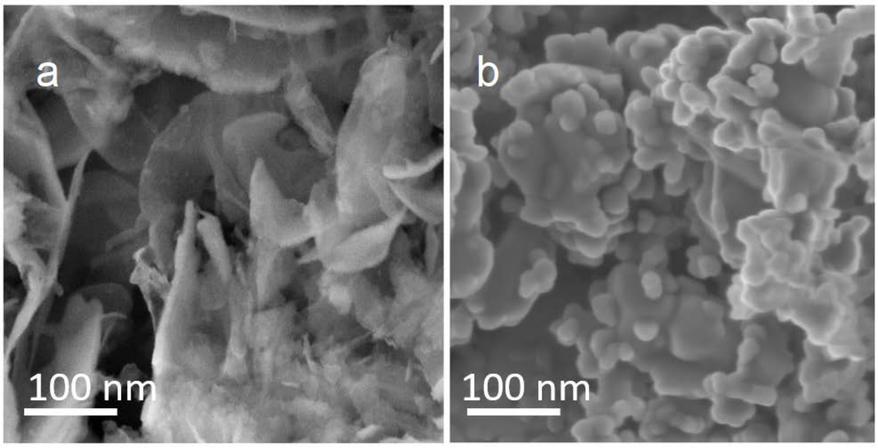

Fig. 2 – The SEM images of (a) MgAlLDH and (b) LDH850.

The nitrogen adsorption isotherms of MgAlLDH, and LDH850 are shown in Fig. 3.

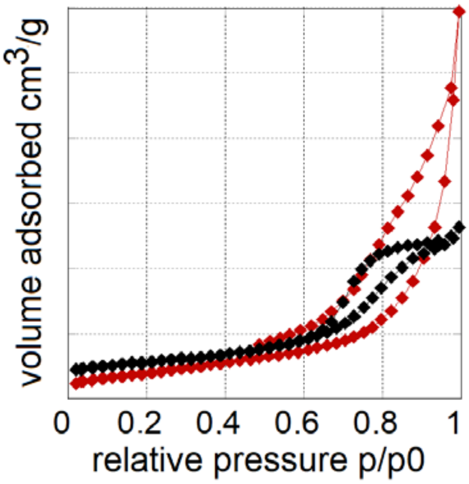

Fig. 3 – The adsorption-desorption isotherms of:
(🟥) MgAlLDH and (⬛) LDH850.

The different appearances of MgAlLDH and LDH850 suggest the modifications of the nano/micro texture as a result of the calcination processes. For MgAlLDH we observe a type IV isotherm with a broad type H3 hysteresis loop, in the middle range of relative pressure. At low relative pressure the prevailing process is the formation of a monolayer while a multilayer adsorption takes place at a high relative pressure. For the values of relative pressure higher than 0.8 condensation takes place giving a sharp adsorption volume increase. This behaviour indicates that this sample has a mesoporous character. Hysteresis loop type shows that aggregates of plate-like particles, forming enough nonuniform slit shaped pores (Sing, 1985), are defining the nanotexture in this sample. For LDH550 and LDH850 the shape of the curves is typical for a type IV adsorption isotherm and a type H_1 hysteresis. The isotherm form and the narrow hysteresis loop, with almost parallel adsorption and desorption branches, indicate that cylindrical pores with mesopore size range and almost regular geometry, more uniform in size and/or shape than those present in MgAlLDH, exist in the calcined LDH. Such that:

- for $p/p_o<0.2$, the multilayer adsorption is revealing microporous characteristics for this sample.

- for $0.2< p/p_o<0.8$, the isotherm shape reveals the presence of mesopores with a wide size range.

- for $p/p_o>0.8$, it can be assimilated with a type II isotherm, characteristic for adsorption in pores with sizes larger than50 nm. These features allow us to conclude that, after the calcination, both microporous and mesoporous properties contribute to establish the adsorption properties.

Adsorption studies through the effect of the initial concentration of the industrial dye

To study the effect of NN concentration on MgAlLDH, we have plotted the adsorbed quantity variation as a function of Ci, ranging from 50 to 400 mg/L (see Fig. 4a). The results show that the adsorbed amount of NN increases with increasing initial concentration. This can be explained by increasing the dye transfer rate at a higher initial concentration, which subsequently causes the adsorption of several dye molecules (Bouberka *et al.*, 2005).

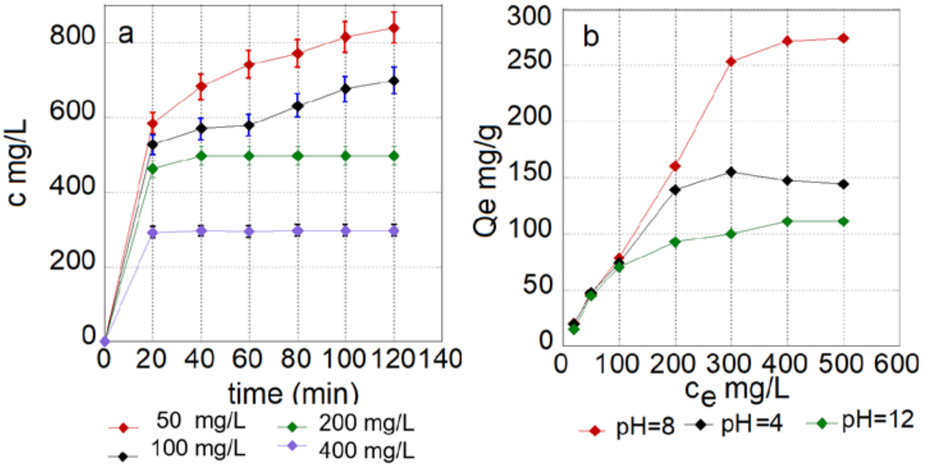

Fig. 4 – (a) Effect of NN concentration as a function of time for MgAlLDH (b) Qe adsorption, as a function of pH, for LDH850.

Adsorption studies through the effect of the pH of the aqueous solution

One of the most critical parameters in the adsorption process of NN from aqueous solutions is the pH of the aqueous environment (Lazaridis and Asouhidou, 2003). The initial pH of the adsorption medium is related to the adsorption mechanisms onto the adsorbent surface from water and reflects the nature of the physicochemical interaction of the species in solution and the adsorptive sites of the adsorbent. The standard range of pH in water varies from 4.5 to 9 and therefore the investigation of the effect of a wide range of pH on NN removal is needed. Hence, the effect of initial pH on the uptake capacities of NN on LDH850, at room temperature, is shown in Figure 4b. In this work the pH range studied was between 4.0 and 12.0. Results reveal that the adsorption capacity decreases for basic pH, while the maximum adsorption capacity was obtained at pH=8, this means almost neutral pH. For LDH550 the results were enough similar to that obtained for LDH850. This behaviour is enough similar to that reported by Zubair *et al.* (2017) Interestingly, after 12 hours of adsorption treatment the pH of the aqueous solution was equilibrated to almost neutral pH, due to the presence of the adsorbent. This is further pointing out the role of the basic LDH-like clay to optimise the pH of the aqueous mediums.

4. Conclusions

Nowadays, water resources are threatened by an increasing number of dangerous pollutants requiring to put forward efficient remediation technologies. In this context, adsorption is among the most efficient and versatile method due to the exploitation of new adsorbents of novel low-cost materials with high adsorption features. Results reveal that MgAlLDH and the mixed oxides, derived after calcination, demonstrated high adsorption efficiencies to remove the industrial dye from the aqueous solutions and the highest removal efficiency, equal to 87%, is reached for LDH850. The micro/nano morphology characteristics of the studied LDH-type adsorbents were tailored using calcination temperatures as a controlled parameter. The concentration of the dye and pH of the aqueous solution were important variables to tailor the adsorption performances.

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HIDROXIZI DUBLU LAMELARI CA MATERIALE ACTIVE DE CURĂȚARE A APELOR POLUATE

(Rezumat)

Problemele de poluare a mediului sunt o preocupare majoră a zilele noastre și în special privind contaminarea apei cu compuși organici toxici. Utilizarea tehnologiilor performante de adsorbție constituie un instrument util în reducerea poluării apei datorită condițiilor blânde cerute de procesul de adsorbție și a performantei sale în procesele de îndepărtare a poluanților. Definiți printr-o compoziție chimică versatilă, hidroxizii dublu lamelari (LDH) pot fi fabricați pentru a fi definiți de nanoarhitecturi specifice, de aceea sunt propuși în prezent ca agenți de curățare eficienți a mediului. Această lucrare prezintă MgAl-CO_3 cu caracteristici nanoarhitectonice specifice pentru a fi folosite ca instrumente eficiente pentru tratarea mediilor apoase poluate cu coloranți industriali (*e.g.*: Nylosan Navy). Rezultatele relevă o legătură puternică între eficiența de adsorbție și caracteristicile micromorfologice ale LDH. Caracteristicile structurale și micromorfologice ale LDH-urilor au fost studiate prin tehnici de adsorbție XRD, FESEM și N_2. Aceste rezultate vor putea permite stabilirea unor noi tehnologii performante pentru a elimina compușii toxici din mediile apoase prin utilizarea LDH-urilor ca agenți eficienți de curățare a apelor poluate cu compuși toxici.