



## Research paper

# X-ray coupled Laser Desorption Ionization assessment of layered double hydroxides for nitrate adsorption based on ion size, affinity and compromised layer height



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## ARTICLE INFO

## Article history:

Received 21 September 2016

Received in revised form 13 February 2017

Accepted 16 March 2017

Available online 27 March 2017

## Keywords:

Nitrates  
adsorption  
MALDI  
Layered double hydroxides (LDH)

## ABSTRACT

The adsorption of nitrates with  $\text{NO}_3(\text{aq})$  solutions ranging from 20 mg/L to 400 mg/L with Layered-Double-Hydroxides (LDH) PURAL 70 (Mg70) and an Erbium containing LDH (Er40) were investigated. The X-ray Diffraction measurements (XRD) are accompanied by complemented Matrix Assisted Laser Desorption Ionization-Time of Flight (MALDI-TOF) measurements for prove of  $\text{NO}_3^-$  containing LDH. The shift in the XRD reflection angle for both Mg70 and Er40 corresponds to MALDI-TOF Data for presence of nitrate for all LDH except for Er40MW, as its nitrate adsorption capacity is the lowest. Both methods show the adsorption of nitrates for microwaved LDH and further calcined LDH, proving the memory effect. UV-vis spectroscopy was used to determine the nitrate concentration. The study shows substantial amount of nitrate adsorption for all LDH. Adsorption ranges from 2 to 5 mg- $\text{NO}_3(\text{aq})/\text{g-LDH}$  for initial  $\text{NO}_3(\text{aq})$  concentration from 20 mg/L to 400 mg/L. Leaching of element from the LDH structure is done by ICP-MS measurements to guarantee no further pollution of environmental waters with mentioned elements. Leaching for Mg ranges from 170 to 1600 mg/m<sup>3</sup> and Al, Er and Fe leaching is less than 10 mg/m<sup>3</sup>.

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## 1. Introduction

The North German territory of Lower Saxony and Bremen are facing the difficulties of increased nitrate concentration in their aquatic environments, caused by over-fertilization (Umweltbundesamt, 2015a). Nitrates are feared to be carcinogenic and lead to eutrophication of mentioned environments (Umweltbundesamt, 2015a, b).

Subsequent measures must be adopted in the least time possible to control further pollution of these environments. Layered double hydroxides (LDH) are known to help reduce nitrate contamination in natural-water environments (Torres-Dorante et al., 2008). Hosni et al. and Torres et al. have fortunately made investigation akin to this report (Hosni and Srasra, 2008; Torres-Dorante et al., 2008), however with other selected layered double hydroxides. Microwave methods for removal of excess  $\text{H}_2\text{O}$  and hydroxyl groups, which are of most abundance

in the LDH, seem to be reasonable and economic to solve this environmental risk in short time (Cross et al., 2012).

The microwave treatment only removes the excess  $\text{H}_2\text{O}$  and the integrity of the layered structure remains. In this case, the cratering effect by  $\text{CO}_3^{2-}$  by calcination is minimized due to the specific targeting of the microwave treatment to remove excess  $\text{H}_2\text{O}$  and leave OH-groups in the brucite-layered structure (Meyer, 2011; Cross et al., 2012).

Hence, the layered structure is preserved but however, the adsorption capacity may suffer. Hosni and Srasra (Hosni and Srasra, 2008) mentioned high nitrate adsorption of calcined LDH and retrieval of the brucite-layer by the memory-effect. However, Torres-Dorante et al. (Torres-Dorante et al., 2008) reported the nitrate adsorption of uncalcined LDH. The discrepant amount of nitrate adsorption by uncalcined and calcined LDH is the aim of this report. This is due to the competitions of ions involved and the layer height of the LDH of this report (Wan et al., 2012).

The competition between nitrate and other ions, such as  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$  and  $\text{NO}_3^-$  has to be addressed, as they are present in groundwater and affect the nitrate adsorption capacity depending on their affinity to the

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adsorption/ion-exchange sites. The affinity to the sites decreases in the order by  $\text{CO}_3^{2-} > \text{SO}_4^{2-} > \text{OH}^- > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^- > \text{I}^-$  (Meyer, 2011). As observed, the nitrates have the lowest affinity compared to other ions, especially doubly-charged ions. The investigation starts with the usual suspects in the microwaved LDH to hinder nitrate adsorption, which are  $\text{OH}^-$  and  $\text{CO}_3^{2-}$ . Further complexity to the adsorption capacity will follow.

Furthermore, the ion size may affect the adsorption capacity by simply having steric hindrance with consideration to the layer height of the LDH of concern (Meyer, 2011; Wan et al., 2012). All the effects mentioned play an important role in this investigation.

The Matrix-Assisted Laser Ionisation/Desorption (MALDI) with detection by time-of-flight mode (MALDI-TOF) may shed light to the characteristics of the LDH before (microwaved) and after calcination and nitrate adsorption in the presence of foreign ions aforementioned.

MALDI-TOF is complementary of determining adsorbed ion in calcined and uncalcined (microwaved) LDH through adsorption of nitrates in the presence of  $\text{CO}_3^{2-}$ . The amount adsorbed correlates to the layer height of the LDH. In this case, the XRD method prevails in determining the layer height.

## 2. Procedure

### 2.1. Experimental section

#### 2.1.1. Nitrate adsorption

**2.1.1.1. Preparation of solution.** A stock nitrate solution with a concentration of 1000 mg/L was prepared by dissolving 1.64 g of  $\text{KNO}_3$  in 100 mL of distilled  $\text{H}_2\text{O}$ . Two sets of four 20 mL solutions were diluted to a range of 20 mg/L to 400 mg/L respectively and placed in 40 mL test tubes (B020, B050, B200, B400). One set is used for nitrate adsorption with a time of 4 h (e.g. B020-S) and the other set serve as reference solutions (e.g B020-R). The nitrate concentration was increased to 400 mg/L due to neutral pH conditions. The system deserves a higher driving force to accommodate to the higher ion exchange capacity at slightly higher groundwater pH-value of around 8 to 8.5. Nevertheless, a lower value of 20 mg/L is also considered.

For UV-vis measurement purposes, the solutions were diluted 100 times again (C020-C400). This is done due to limitations of Navone's method to perform well to a maximum  $\text{NO}_3^-$ -concentration of 8.8 mg/L (Navone, 1964). 200  $\mu\text{L}$  of each solution was diluted in 19.8 mL of distilled  $\text{H}_2\text{O}$ . This was again done twice for both sets of sample (S) and reference solutions (R) (B020-S to B400-S and B020-R to B400-R). 200 mg of prepared Zinc-Copper couple is added to the one set of C020-R/S to C400-R/S solutions (Navone, 1964). It is to suppress nitrate concentration in the reference and sample solutions and freely measure nitrate concentration without interference other ions in the solutions. The rest of the B020-S to B400-S solutions are taken for ICP-MS measurement for leaching analysis for the elements of Magnesium (Mg), Aluminium (Al), Iron (Fe), and Erbium (Er) originating from the LDH.

**2.1.1.2. Preparation of solid phase.** Mg70 is a commercial hydroxy-carbonate based hydrotalcite from SASOL named PURAL. It has a  $\text{MgO}:\text{Al}_2\text{O}_3$  ratio of 70:30, whereas Er40 is a hydroxy-carbonate based hydrotalcite already synthesized by Meyer (Meyer, 2011). It has a base  $\text{MgO}:\text{Al}_2\text{O}_3$  ratio of 85:15 and Er40 being 40% of the Aluminium being substituted by Erbium. Both are brucite layered structures. Carbonate based LDH are studied to investigate the  $\text{NO}_3^-$ -adsorption capacity in the presence of carbonate and hydroxyl ions, as these LDH are reported to have a higher affinity to  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  than to  $\text{NO}_3^-$  (Hosni and Srasra, 2008, 2009; Meyer, 2011).

Data for Mg70 (PURAL Mg70) and Er40 are readily available as literature data. Mg70 was purchased from SASOL and the necessary data required is provided by the respective company. The syntheses of the Er40

sample and its respective characterization has already been done by Meyer (Meyer, 2011).

It is recommended to take LDH with mid-range  $\text{NO}_3^-$  adsorption capacity. Even if higher adsorption capacity are reported by Hosni et al. and Torres-Dorrante (Hosni and Srasra, 2008; Torres-Dorrante et al., 2008), it is important to attain reasonable data by LDH with mid-range  $\text{NO}_3^-$  adsorption capacity. This hence proves feasibility of LDH to be used as a potential adsorbent in this case. This proves the feasibility of LDH with high adsorption capacity by default. A portion of 5 g of each LDH was treated by means of a Samsung microwave at 850 W for 8 and 12 min. Calcination of the sample is done at 420 °C for 6 h (Meyer, 2011). Formation of oxides is confirmed by XRD analysis for the calcined samples (for XRD data of calcined LDH form see Supporting information).

**2.1.1.3. Adsorption experiment.** Sample names (Mg70 or Er40) are given by their treatment process (MW or MWC) and  $\text{NO}_3^-$  concentration in solution (020 for 20 mg/L to 400 for 400 mg/L). An example is Mg70-MW-020 where the LDH concerned is the LDH with 70w% of magnesium hydroxide in the brucite layer, microwave treated and treated with an aqueous nitrate solution of 20 mg/L (see Table 1). To compensate for the soil pH of 8.5, a higher amount LDHs were used compared to works of Hosni et al. and Dorres-Torrante et al. (Hosni and Srasra, 2008; Torres-Dorrante et al., 2008).

200 mg of microwave treated (MW) and further calcined (MWC) LDH were added to 1 set of the 4 sample test tubes B020-S to B400-S. The solutions are shaken for 4 h. The solid phase is filtered and microwaved for 12 min again to remove excess water. This corresponds to the water release of all LDH concerned in this report (see TGA experiments in Supplementary Information). The filtered supernatant solution is taken for UV-vis and ICP-MS measurements. MALDI-TOF and XRD analysis were done for the dried solid phase.

#### 2.1.2. Phase analysis by XRD

XRD measurements with Copper  $\text{K}\alpha$ -source in reflective mode measurements were done before and after microwave treatment (Mg70-8/12 MW, Er40-8/12 MW) measurements and for all samples introduced to the nitrate solution (LDH-MW-020-400 and LDH-MWC-020-400).

The phase analysis of LDH gives a reflex at 10–12° in the diffractogram. This corresponds to the 001 basal plane of the respective LDH. This corresponds to the layer height of the LDH.

There exists a combined effect of the partial substitution of  $\text{Al}(\text{OH})_6^{3-}$  as by  $\text{Er}(\text{OH})_6^{3-}$  and further  $\text{Er}_2\text{O}_3$ -clusters on the layer surface at excess of Erbium precursor during synthesis (Meyer, 2011). Upon removal of additional OH-groups by calcination, rehydration and further microwaving, two distinct reflexes are observed in this case.

The cation size of Erbium and Magnesium is similar and allows for proper substitution without distortion of the layer height. The cation size of potassium may distort the layer upon treatment with nitrate solutions (see Table 2). This is due to the preparation of the nitrate solution by  $\text{K}_2\text{CO}_3$  (see section 2.1.1). The incorporation of the cation in the lattice is less possible as this would distort the layer structure and the reflex at 10–12° may disappear, which is not observed in this investigation. Cluster formation due to  $\text{K}_2\text{O}$  may also be possible. However, this is not observed, as two distinct peaks in Mg70-MW and Mg70MWC is absent.

**Table 1**

The designation of samples used in this report.

Sample name	Microwaved sample (uncalcined)	Microwaved and calcined sample	$\text{NO}_3^-$ -concentration
Mg70	MW	MWC	020-400
Er40	MW	MWC	020-400

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