



Impacts of multi-pollutants on sulfonamide antibiotic removal from water matrices using layered double hydroxide sorbents

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ABSTRACT

Remediation of sulfamethoxazole (SMX) present in the aqueous environment requires the development of new advanced wastewater treatment technologies, crucial to reduce the toxicity of such pollutants to the environment, supporting urban water reuse. Continuously synthesised layered double hydroxides (LDH) have been applied as a sorbent material for the removal of SMX from water. No equilibrium uptake of SMX was observed from any water matrix. However, an unusual sorption/release behaviour of SMX was observed in the presence of Mg₂Al-NO₃-LDH, influenced by the characteristics of the water matrix. A maximum SMX removal percentage of 34.7% was reached within 10 min, from ultrapure water, followed by release of SMX back into solution over the following 24 h. Further, Mg₂Al-NO₃-LDH is shown to release NO₃ into all water matrices. It is proposed that NO₃ disrupts the SMX-LDH interactions, resulting in release of SMX from the LDH. No initial SMX sorption was observed onto Mg₂Al-NO₃-LDH when wastewater effluent was the water matrix, likely due to competition for sorption sites on the LDH with multiple pollutants, including metals and additional anionic nutrients, present in the wastewater. This work illustrates the potential for relationships between the sorbent material and water matrix interactions on pollutant sorption behaviour. In addition, the findings highlight the importance of conducting removal experiments at realistic environmental conditions to ensure development of suitable sorbent materials for pollutant remediation.

1. Introduction

Widespread consumption of antibiotic pharmaceuticals, coupled with human activities, has resulted in environmental contamination. The presence of antibiotics in the aqueous environment is of global concern, linked to environmental toxicity and contributing to the spread of antimicrobial resistance (Chow et al., 2021; Felis et al., 2020; Wellcome Trust, 2018). Antibiotics are classed as emerging contaminants, as yet unregulated pollutants, that are not sufficiently removed by current wastewater treatment processes (WWTP) (Rasheed et al., 2019). Therefore, advanced treatment technologies are required for antibiotic removal to support urban water reuse.

Sorption has been applied for the antibiotic removal from water matrices, due to its considerably low operational cost, simple set-up and range of sorbent materials available (Khan et al., 2022; Rathi et al., 2021). Layered double hydroxides (LDHs) are often cited as suitable candidates for sorption of many conventional pollutants such as dyes (Johnston et al., 2021; Yang et al., 2016), metals (Liang

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et al., 2013), phosphate (Benhiti et al., 2020) and other oxyanions (Goh et al., 2008). LDHs are inorganic materials with highly tuneable structures with the chemical formula $[M_1^{2+}_x M_2^{3+}_x (\text{OH})_2] (\text{A}^n)_{x/n} \bullet m\text{H}_2\text{O}$, in which various metals (M) and charge balancing anions (A^n) can be incorporated into the structure (Cavani et al., 1991). There are many options for the synthesis of LDH, including commonly used batch synthesis approaches including coprecipitation, urea hydrolysis, and reconstruction (Wang et al., 2023). Additionally, continuous hydrothermal flow synthesis can be used for the production of LDH at different manufacturing scales (Clark et al., 2019). Beyond use as sorbent materials, LDHs have gained interest for use in diverse applications, including for soil amendment (Mao et al., 2022), as catalysts (Fan et al., 2014), within drug delivery systems, and as antimicrobial materials (Mishra et al., 2018).

The suitability of LDHs for sorption applications rely on their properties including relatively high surface areas and anion exchange potential. Whilst it has been proposed that LDHs may be appropriate for the remediation of antibiotics from water matrices, studies focusing on antibiotic removal remain sparse (Johnston et al., 2021). Pharmaceuticals differ from conventional pollutants as they are heterogenous chemicals with disparate chemical functional groups present, and therefore varied sorption behaviours can be expected (Harrower et al., 2021; Patel et al., 2019). To date research has focused on LDH removal of antibiotics from two of the seven major classes of antibiotics, tetracyclines (e.g. tetracycline (Gao et al., 2022), oxytetracycline (Eniola et al., 2020) and doxycycline (Moaty et al., 2019)) and fluoroquinolones (e.g. ciprofloxacin (Gao et al., 2022) and norfloxacin (Sui et al., 2012)). This may be rationalised through the greater affinity of antibiotics from these classes for sorption on to soils and natural clays, when compared to compounds from other antibiotic classes (Harrower et al., 2021). The omission of evaluating the sorption of a wider range of antibiotics is limiting the understanding of how applicable LDHs may be in the removal of a wide variety of antibiotics from water.

Sulfamethoxazole (SMX) (Supplementary Information, Table S1), a broad-spectrum sulfonamide antibiotic, has been identified as one of the most concerning antibiotics present in the environment, requiring enhanced monitoring, risk management and remediation (Gomez Cortes et al., 2020; Yang et al., 2022). Significant global consumption of SMX, alongside the prolonged half-life of SMX in aqueous environments, results in frequent detection of SMX globally (Baran et al., 2011). Concentrations up to 39 $\mu\text{g}/\text{L}$ of SMX have been recorded in rivers in urban Kenya (K'oreje et al., 2016), and up to 49 $\mu\text{g}/\text{L}$ and 1340 $\mu\text{g}/\text{L}$ have been observed in effluent from pharmaceutical manufacturing facilities (Khan et al., 2013; Lin and Tsai, 2009). Despite this, only one example in the literature is known for the removal of SMX by an unmodified-LDH (Li et al., 2019). Additionally, removal of SMX by a calcined ZnAl-LDH is reported, however sorption mechanisms through reconstruction of the calcined LDH are distinct to sorption mechanisms onto unmodified-LDH (Mourid et al., 2019).

There is also an absence of studies considering pharmaceutical removal from environmental water matrices, compared to removal from laboratory-grade water (Johnston et al., 2021). Environmental water matrices, from surface water to wastewater effluent (WWE), contain a wide array of components which may have antagonistic consequences on a materials sorption performance. The complexity and variability in environmental water matrices will influence and provide variations in sorption performance for pharmaceutical removal, as reported for SMX removal from laboratory-grade water versus environmental water matrices by alternative sorbent materials (Huang et al., 2020; Silva et al., 2019). The lack of sorption studies under realistic environmental conditions has been highlighted in the case of organoclays, whilst the complexity of electrolyte competition is well established in the case of clay minerals (Guégan et al., 2020). Similar observations can be hypothesised for LDH sorbent materials, due to their similarly layered clay-like structure.

This study investigates SMX behaviour in the presence of $\text{Mg}_2\text{Al-NO}_3$ -LDH. Ultrapure water, anion-doped ultrapure water, and SMX-spiked WWE were each evaluated as the water matrices. Results show SMX behaviour to be greatly impacted by water matrix properties, with no equilibrium uptake of SMX by LDH observed across all experimental conditions. Furthermore, it is revealed the LDH itself is impacting the water matrix through release of nitrate. This is found to have unintended effects on SMX sorption behaviour, speculated to result in the spontaneous release of SMX from the LDH. The direct relationship between the water matrix and pollutant behaviour strengthens the argument that evaluation of sorbent materials should be carried out in environmental water matrices early in the development process of new sorbent materials.

2. Materials and methods

2.1. Chemicals and reagents

Information about the chemicals used throughout this work are presented in Text S1 (Supplementary Information). Laboratory-grade (ultrapure) water (18.2 $\text{m}\Omega$) was used throughout all experiments, unless otherwise stated.

2.2. Preparation and characterisation of LDH

A continuous hydrothermal synthesis approach was utilised for the synthesis of all LDH used in this study. The reactor arrangement used is as previously reported (Lester et al., 2006). Synthesis conditions used were based on previously reported protocols (Wang et al., 2013; Williams et al., 2019). Further information regarding LDH synthesis is presented in Text S2 (Supplementary Information), with specific reaction conditions for each LDH synthesised shown in Table S2 (Supplementary Information). Details on LDH characterisation can be found in Text S3 (Supplementary Information).

2.3. SMX sorption from water matrices

The removal of SMX by various LDH was investigated through a batch experiment set-up. Typically, powdered-LDH (200 mg) was

dispersed into 250 mL of SMX solution of known concentration (typically 100 µg/L) in a 500 mL conical flask, foil-wrapped to avoid photodegradation. Sorption experiments were performed through continuous stirring of the reaction medium in an incubator at a pre-determined temperature ranging from 10 to 30 °C, for between 24 and 72 h. At set time intervals, a 1.5 mL aliquot of the reaction media was transferred from the reaction flask to a 2 mL Eppendorf. The 1.5 mL samples were then centrifuged for 3 min at 13400 rpm to separate out the solid LDH, and 1 mL of the supernatant was transferred to amber vials and stored at 4 °C prior to analysis (maximum of 18 h). Control experiments confirmed no degradation of the SMX over experimental time frames (Supplementary Information, Figure S1), further confirmed by literature reports (Białk-Bielińska et al., 2012).

In the case of experiments in which the LDH samples were pre-dispersed in ultrapure water before addition of SMX, all experimental conditions were as above apart from the order of SMX and LDH addition to the water matrix. Powdered-LDH (200 mg) was dispersed into 250 mL of ultrapure water and stirred in an incubator at 20 °C for 1.5 h. 1.25 mL of reaction media was then removed and replaced with 1.25 mL of a 20 mg/L SMX in MeOH. Aliquots were then taken from the reaction media at set time points to allow for quantification of SMX. As it is not possible to accurately quantify $t = 0$ h SMX concentration before exposure to LDH this is estimated to be 100 µg/L for all relevant SMX removal calculations.

A 1 g/L stock solution of SMX was prepared in High Performance Liquid Chromatography (HPLC)-grade MeOH in an amber vial and stored at -20 °C. Working stock solutions were made as required from the stock diluting to 20 mg/L in MeOH before being further diluted to required concentrations in ultrapure water.

2.4. Quantification of sulfamethoxazole

The concentration of the SMX in ultrapure water was quantified by HPLC with ultraviolet spectroscopy. SMX concentration quantification was carried out using a matrix matched 6-point calibration curve (20 – 125 µg/L). The concentration of SMX in WWE was quantified using both HPLC-UV and liquid chromatography tandem mass spectrometry (LCMS/MS). Quantification was carried out using a 7-point calibration curve (0.5 – 110 µg/L). SMX quantification was found to be consistent when replicated on LCMS/MS and compared with data collected from HPLC-UV analysis. Further details of analytical methods are included in Text S4 (Supplementary Information).

The sorption performance of the LDH for the removal of SMX was calculated through removal percentage. Removal percentage (% R) is calculated as follows:

$$\%R = \frac{C_0 - C_t}{C_0} \times 100$$

Where C_0 (mg/L) is the initial SMX concentration in solution and C_t (mg/L) is the SMX concentration in solution at a given time. Unless otherwise highlighted, experiments were carried out in triplicate with SD errors shown.

2.5. Wastewater effluent sampling and characterisation

Wastewater effluent (WWE) was collected from Stoke Bardolph WWTP (Nottinghamshire, UK). The WWTP serves a population equivalent of ~750,000, utilising a mixture of conventional and advanced activated sludge. Sampled WWE was filtered through 1.2 µm pore size micro glass fibre filter paper (Fisher Scientific, Loughborough, UK) prior to characterisation and application in removal experiments. Water quality parameters are shown in Table S3 (Supplementary Information). Filtered WWE was used in sorption experiments to minimise additional sorption or degradation of the pollutant resulting from the presence of suspended solids (Aminot et al., 2018). Experiments were commenced within 4 h of WWE sampling to decrease the impact of natural changes to the WWE on experimental outcomes.

2.6. LDH stability and impact on water matrix

To consider the impact the LDH and the water matrix may be having on each other, both components were characterised following both sorption and control experiments. Typically, 2 g/L of LDH was stirred in 50 mL ultrapure water at 20 °C for 24 h. The pH was monitored at set time points across the duration of the experiment. For monitoring nitrate in solution, 2 mL of reaction media was removed from the flask at set time intervals and centrifuged for 5 min at 13400 rpm. The nitrate concentration of the supernatant was quantified photometrically using a Hach DR 2800 Spectrophotometer (Manchester, UK) and LCK339 or LCK340 Hach tests, with NO_3^- concentration analysis ranges of 1–60 mg/L and 22–155 mg/L respectively. Metal concentrations in solution were quantified after 24 h. 50 mL of solution was centrifuged at 4000 rpm for 20 min, the supernatant was then passed through a 0.45 µm polyethersulfone (PES) syringe filter (Camlabs, UK) and acidified to a 2% v/v nitric acid concentration and stored at 4 °C prior to analysis. An Agilent 5110 Vertical Dual View instrument (Ca, USA) with 240 place SPS-4 autosampler was used for quantification of Al and Mg in solution. Instrument operation and data processing was carried out via Agilent 'ICP Expert' software package. For experiments in which the solid LDH sorbent material was recovered for characterisation, the remaining reaction media was centrifuged at 4000 rpm for a minimum of 5 min in 50 mL aliquots. The solid LDH was isolated via decanting supernatant and subsequently dried in an oven at < 75 °C for minimum of 4 h. The residual solid was then carefully crushed for further characterisation by pXRD and FT-IR.

3. Results and discussion

3.1. SMX behaviour in the presence of Mg_2Al-NO_3-LDH in ultrapure water

The concentration of SMX in ultrapure water in the presence of Mg_2Al-NO_3-LDH decreased during the initial 45 min contact time, reaching a maximum SMX removal of $35.6 \pm 4.83\%$. After 45 min, desorption of SMX from the LDH into solution was observed, resulting in only $0.38 \pm 3.61\%$ SMX removal from ultrapure water at 48 h (Fig. 1a). Monitoring SMX concentration in solution over an additional 24 h (up to 72 h contact time) showed no change in the SMX concentration in the water matrix. This indicated there is an initial sorption mechanism of SMX onto the LDH, followed by disruption of this interaction resulting in SMX release back into the water. Throughout, unless otherwise stated, a Mg_2Al-NO_3-LDH is used, more details of the material are presented in Text S5 and Figure S2 (Supplementary Information.).

Multiple sorption mechanisms are cited for the removal of organic pollutants from water matrices by LDH, including electrostatic interactions; interlayer anion exchange; and surface adsorption (for example H-bonding) (Yang et al., 2016). The pH of the water solution can give insights into the feasibility of such sorption mechanisms through understanding pollutant speciation and LDH surface charge. Solution pH was monitored throughout the removal experiments, with a maximum solution pH 9 reached, stabilising from 45 min onwards between pH 8–8.5 (Fig. 1b), illustrating the widely reported buffering capabilities of LDH (Liu et al., 2022; Macedo-Miranda et al., 2022). Sulfamethoxazole can be present in solution in a cationic, zwitterionic or anionic form depending on solution pH, characterised by two acid dissociation constants, pK_{a1} , 1.8; pK_{a2} , 5.6 (Supplementary Information, Figure S3) (Babić et al., 2007). With a solution pH > 7, SMX will be present primarily in an anionic form in the presence of Mg_2Al-NO_3-LDH . As the pH_{PZC} of Mg_2Al-NO_3-LDH is calculated to be 10.04, in agreement to previously reported values, the LDH surface will be positively charged (Supplementary Information, Figure S4) (Goh et al., 2008). Considering the opposing charges of SMX and the LDH surface in solution, the initial SMX sorption may result from favourable electrostatic interactions between the SMX anions and positively charged LDH surface. Similar behaviour is reported for the sorption of amoxicillin onto $MgAl-LDH$ (Elhaci et al., 2020) and levofloxacin onto $ZnAl-LDH$ (Mahgoub et al., 2020). Alternatively, sorption may occur through interlayer anion exchange between the anionic SMX ions

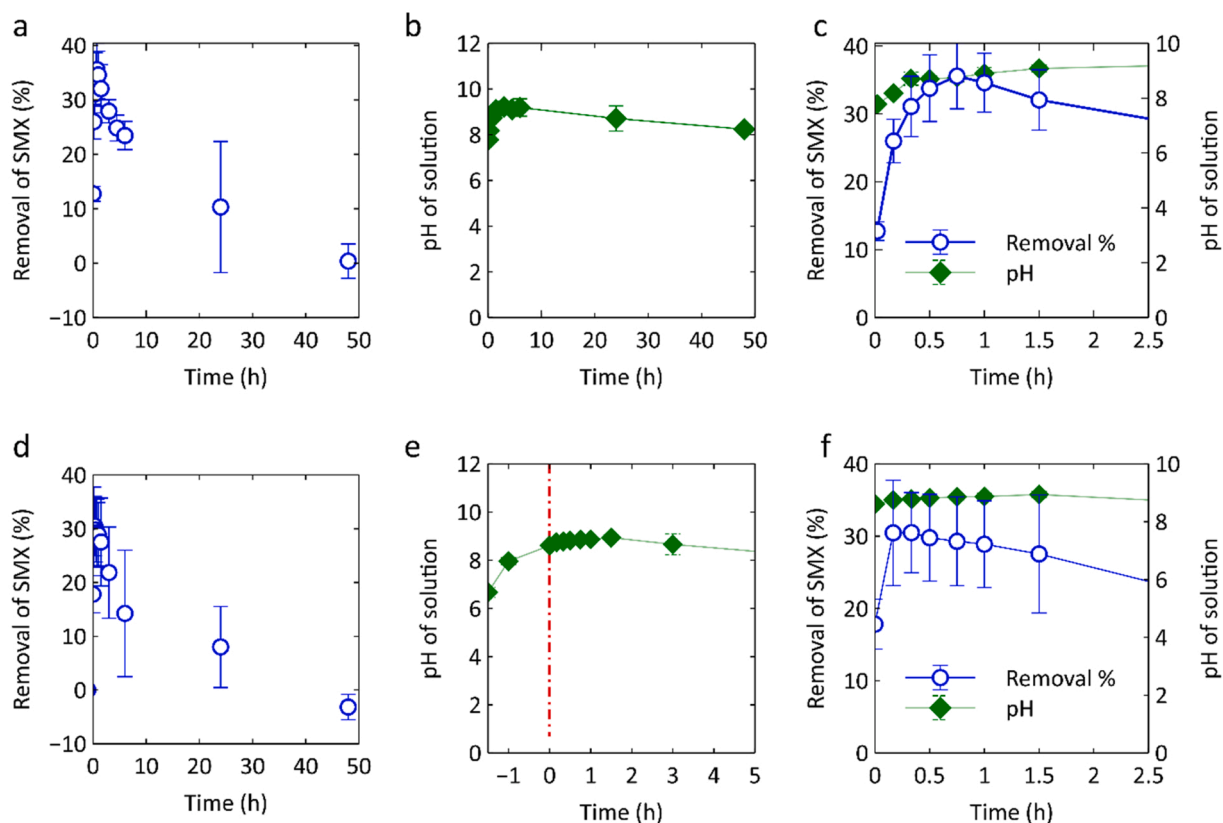


Fig. 1. (a) Removal percentage of SMX over time (0 – 48 h) in presence of Mg_2Al-NO_3-LDH in ultrapure water (b) Solution pH over course of removal reaction in ultrapure water (c) Overlay of removal percentage of SMX over time (0 – 2.5 h) and solution pH in ultrapure water (d) Removal percentage of SMX following pre-addition of Mg_2Al-NO_3-LDH to ultrapure water over time (0 – 48 h) (e) Solution pH following addition of Mg_2Al-NO_3-LDH to ultrapure water at $t = -1.5$ h, with $t = 0$ h (red line) indicating point of SMX addition (f) Overlay of removal percentage of SMX over time (0 – 2.5 h) and solution pH following pre-addition of Mg_2Al-NO_3-LDH to ultrapure water. Reaction conditions: $[SMX] = 100 \mu g/L$, $[LDH] = 0.80 g/L$, $T = 20^\circ C$, continuous stirring.

and NO_3^- present in the interlayer spacing of LDH, as observed for diclofenac removal by MgAl-LDH (Mkaddem et al., 2022). Unlike these cited studies, this work observed desorption of SMX after 45 min. Whilst there is an initial favourable SMX-LDH interaction causing SMX removal from the ultrapure water to the LDH material, it is reversible in the absence of an external stimuli, resulting in the release of SMX from the LDH back into the water matrix.

A similar sorption/release behaviour was detected by Wang et al. (2022) in their work investigating SMX degradation by ultrathin- NiAl-LDH . They reported a 78% decrease in SMX concentration in DI water within 1 min of exposure to the LDH. However, the subsequent 1 h observed SMX desorption back into solution resulting in 40% removal of SMX from ultrapure water at 1 h. The study is time limited, and hence an equilibrium SMX removal percentage is not reported. Equilibrium removal of SMX is important to fully understand the SMX-LDH interactions, and as seen in the data collected for SMX concentration in presence of $\text{Mg}_2\text{Al-NO}_3\text{-LDH}$ equilibrium removal was not reached until between 24 and 48 h. Wang et al. (2022) speculate the SMX release could be due to change in LDH zeta potential.

Analogous sorption/desorption behaviour was seen in the sorption of SMX from 0.01 M NaCl deionised water solutions onto an alternative sorbent material, powdered activated carbon functionalised with magnetite particles (Lv et al., 2021). Removal of SMX by the sorbent material is seen in the first 10 min of exposure, however the samples with higher mass ratios magnetite functionalisation on the activated carbon begin to show desorption of SMX into solution after this 10 min contact time. Experiments were conducted for 1 h, with SMX concentrations appearing to be changing at this time point. Therefore, it is unclear what the equilibrium removal percentage of SMX would be if the experiments were continued. Lv et al. (2021) explain the SMX desorption to be a result of potential abrasion of particles releasing magnetite into solution hence release of SMX. However, no further evidence of such particle behaviour is provided, and the same phenomenon was not observed for the activated carbon particles with lower magnetite loadings.

3.2. Implications of solution pH and experimental variables

The desorption of SMX coincided with the stabilisation of solution pH during the removal experiment (Fig. 1c). A key factor in many sorption mechanisms is pH, therefore changes in solution pH during sorption experiments may be disrupting the SMX-LDH interactions (Khan et al., 2022). To monitor this effect, LDH was stirred in ultrapure water for 1.5 h to allow for pH stabilisation, which occurred between 8.6 and 8.9 (Fig. 1e). Fig. 1d shows that following the addition of SMX to the LDH and ultrapure water matrix a sorption/desorption behaviour was observed for SMX. This is similar to that observed for the sorption of SMX without LDH pre-addition, with an initial rapid sorption of SMX to the LDH followed by a more gradual desorption of SMX from the LDH back into solution. This indicates that the pH stabilisation observed in the first experiment is not the key driver behind the sorption/desorption mechanism (Fig. 1f). In the case of pre-addition of LDH, a maximum SMX removal percentage of $30.5 \pm 5.53\%$ was reached, within SD error of the SMX removal percentage without pre-addition of LDH, $35.6 \pm 4.83\%$.

A range of other experimental conditions can impact sorption behaviour of pollutants with LDH, including solution temperature, concentration of pollutant, and concentration of LDH used (Johnston et al., 2021). To exclude the role of such conditions on SMX sorption/release behaviour, removal experiments changing such variables were undertaken (Supplementary Information, Figure S5).

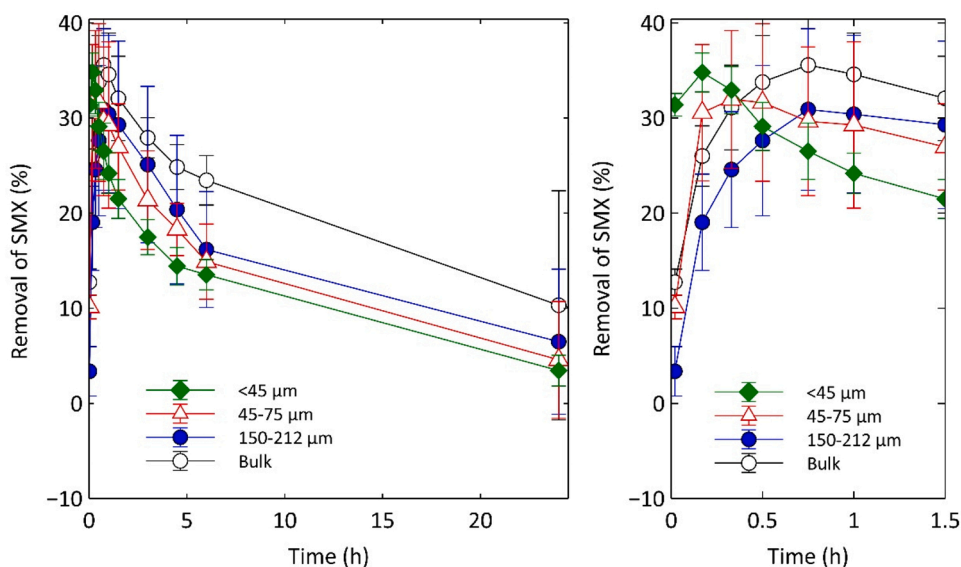


Fig. 2. SMX removal percentage with time 0 – 24 h (left) and 0 – 1.5 h (right) for different $\text{Mg}_2\text{Al-NO}_3\text{-LDH}$ particle sizes, compared to the bulk $\text{Mg}_2\text{Al-NO}_3\text{-LDH}$ sample, from ultrapure water. LDH samples shown are < 45 μm (green diamonds), 45 – 75 μm (red outline triangles), 150 – 212 μm (blue circles), and bulk LDH sample (black outline circles). Reaction conditions: $[\text{SMX}] = 100 \mu\text{g/L}$, $[\text{LDH}] = 0.80 \text{ g/L}$, $T = 20 \text{ }^\circ\text{C}$, continuous stirring. Lines are shown to guide the eye only.

A sorption/release behaviour of SMX was observed under all experimental conditions considered. Therefore, external experimental factors are not directly driving SMX behaviour in the presence of $\text{Mg}_2\text{Al-NO}_3\text{-LDH}$. No obvious trends can be drawn from the data sets, likely due to the nature of the coexisting sorption/desorption mechanisms.

To investigate the potential cause of the standard deviation (SD) values observed in the data sets, three narrow particle sizes of $\text{Mg}_2\text{Al-NO}_3\text{-LDH}$ -bulk were applied in sorption experiments ($\text{Mg}_2\text{Al-NO}_3\text{-LDH}$ -<45 μm , $\text{Mg}_2\text{Al-NO}_3\text{-LDH}$ -45–75 μm and $\text{Mg}_2\text{Al-NO}_3\text{-LDH}$ -150–212 μm). The pXRD patterns collected for each size fraction indicate that the same LDH structure is present in each of the selected size fractions (Supplementary Information, Figure S6). Microscopy images show that the particles are irregular in shape across each of the size fractions (Supplementary Information, Figure S7 and Figure S8).

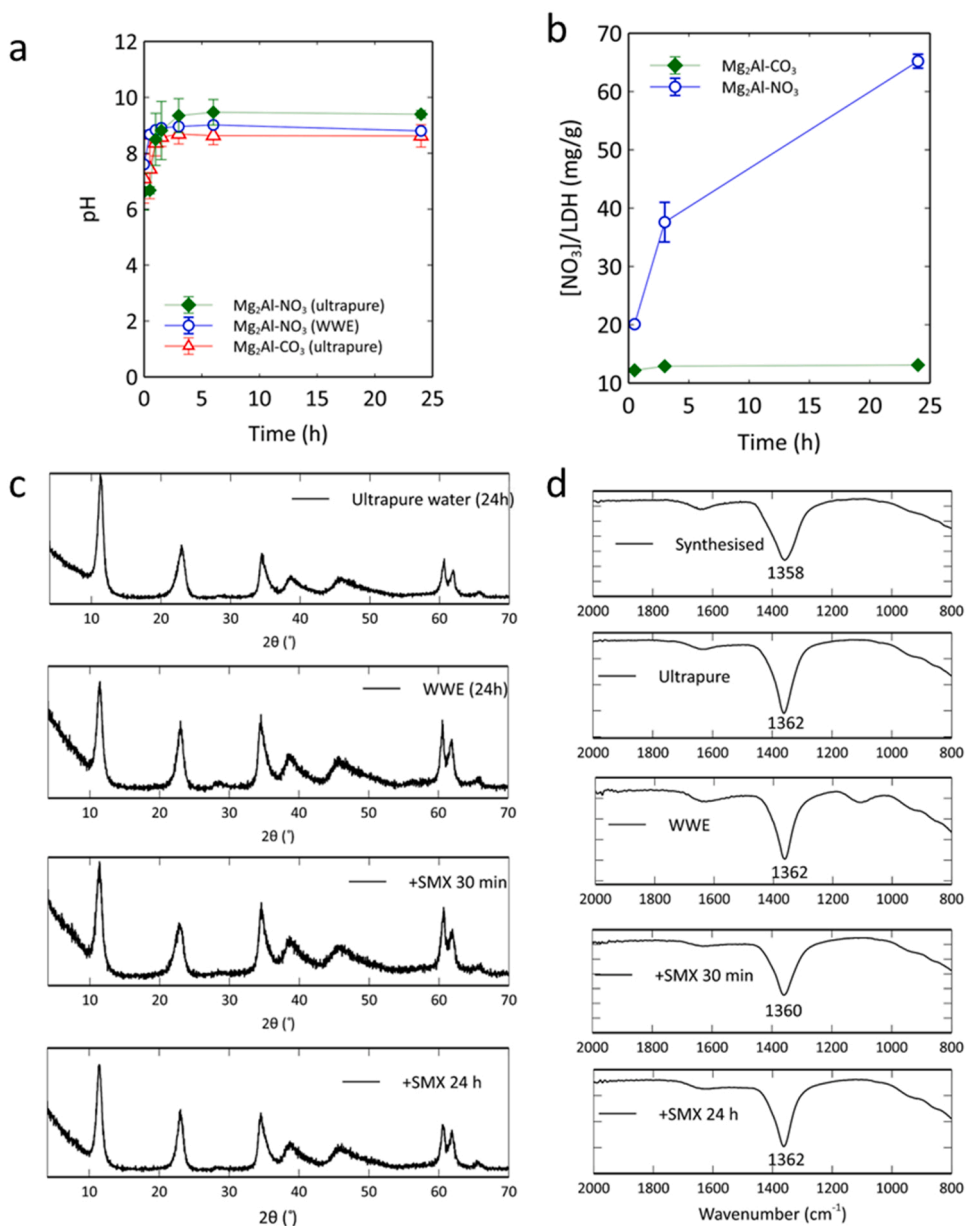


Fig. 3. (a) Change in solution pH between 0 – 24 h on exposure of $\text{Mg}_2\text{Al-NO}_3\text{-LDH}$ sample in ultrapure water (green diamonds), $\text{Mg}_2\text{Al-NO}_3\text{-LDH}$ sample in WWE (blue outline circle), and $\text{Mg}_2\text{Al-CO}_3\text{-LDH}$ sample in ultrapure water (red outline triangle). (b) Solution concentration of NO_3^- in solution per 1 g of LDH at set time points during exposure to ultrapure water. $\text{Mg}_2\text{Al-NO}_3\text{-LDH}$ (blue outline circle) and $\text{Mg}_2\text{Al-CO}_3\text{-LDH}$ (green diamonds). Reaction conditions: $[\text{LDH}] = 2 \text{ g/L}$, $T = 20 \text{ }^\circ\text{C}$, continuous stirring. (c) pXRD patterns of $\text{Mg}_2\text{Al-NO}_3\text{-LDH}$ sample following exposure to (top to bottom) ultrapure water for 24 h, wastewater effluent for 24 h, 100 $\mu\text{g/L}$ SMX for 0.5 h, and 100 $\mu\text{g/L}$ SMX for 24 h. Scale of y axis may vary for clarity. (d) FT-IR spectra between 1000 – 2000 cm^{-1} of $\text{Mg}_2\text{Al-NO}_3\text{-LDH}$ sample following exposure to (top to bottom) as synthesised, ultrapure water for 24 h, wastewater effluent for 24 h, 100 $\mu\text{g/L}$ SMX for 0.5 h, and 100 $\mu\text{g/L}$ SMX for 24 h. Scale of y axis may vary for clarity.

Fig. 2 shows the same sorption/release mechanism of SMX, as observed in the bulk LDH samples, was seen across each size fraction. The maximum removal percentage for the different size fractions showed very small variation, $34.7 \pm 2.05\%$, $31.9 \pm 7.24\%$, and $30.9 \pm 8.49\%$ respectively for the $< 45 \mu\text{m}$, $45\text{--}75 \mu\text{m}$, and $150\text{--}212 \mu\text{m}$ size fractions. Note that the different LDH size fractions will be related to a difference in specific surface areas which may contribute to the variation in maximum removal percentage (Supplementary Information, Table S4). The time taken to reach the maximum removal percentage increased from 10 min to 60 min as the size of the particle fractions of LDH increased. Findings are analogous to the sorption of alternative pollutants, including arsenic and chromium, onto LDH, in which the adsorption rate changed depending on the particle size, whereas no difference was observed for the equilibrium sorption removal capacity (Lazaridis et al., 2004; Yang et al., 2006).

The smallest SD errors are observed for the $< 45 \mu\text{m}$ sample and therefore, $\text{Mg}_2\text{Al-NO}_3\text{-LDH-}< 45 \mu\text{m}$ was carried forward for all further sorption experiments to decrease errors present in the data due to the influence of LDH particle size. This decrease in SD error observed across triplicate experiments is likely a factor of the stability of the suspensions formed of the LDH in the SMX solution. As zeta potentials are greater than $+30 \text{ mV}$, except in the case of $\text{Mg}_2\text{Al-NO}_3\text{-LDH-}150\text{--}212 \mu\text{m}$, it can be expected they will each form stable suspensions (Supplementary Information, Table S4). However, smaller particles are less prone to aggregation or settling following external disruptions to the agitation of solution, explaining the smaller SD errors in the $\text{Mg}_2\text{Al-NO}_3\text{-LDH-}< 45 \mu\text{m}$ sample (Dietrich, 1982).

3.3. Effect of water matrix characteristics on SMX sorption behaviour to LDH

To fully understand the possibility of being able to utilise LDH as a sorbent material for environmental remediation, it is crucial to consider the removal from real environmental water matrices early in the development of the sorbent material. Focussing on removal studies in ultrapure water does not allow for an understanding of how additional components present in complex environmental water matrices may interact with the sorption process.

To investigate the influence of water matrix on SMX sorption onto LDH, WWE was used in place of ultrapure water. A clear distinction between ultrapure and WWE was observed, with no sorption of SMX to the LDH in WWE at $t = 24 \text{ h}$ (Fig. 4). The pH of the WWE stabilised at pH 8.6 (Supplementary Information, Figure S9), similar to that for ultrapure water (8.6 – 8.9), hence charges on the SMX and LDH surface would still allow favourable electrostatic interactions to take place. However, WWE contains a wide range of other constituents, which will likely compete with SMX for the sorption sites on the LDH surface. The complexity of negatively charged dissolved organic matter present in WWE has been shown to compete with the SMX for sorption sites on an Al-modified biochar sorbent material, resulting in decreased removal capacity of the SMX then when compared to ultrapure water (Huang et al., 2020). Competing compounds present in WWE, such as fulvic and humic acids, are rapidly removed from aqueous matrices by MgAl-LDHs reaching 85% removal from a starting concentration of 100 mg/L within 15 min (Vreysen and Maes, 2008). The rapid kinetics associated with the sorption of these compounds will directly outcompete SMX sorption to the LDH surface, supporting the lack of sorption observed for SMX in WWE, due to competition with other components in WWE.

3.4. Changes in LDH structure and water matrix composition

It is apparent that it is crucial to understand how complex and variable water matrices impact sorption performance of pollutants. However, even more seldom considered in sorption studies is the impact on sorbent materials when exposed to aqueous environments. For example, it has been highlighted by Rego et al. (2021) that knowledge is limited regarding the stability of metal organic frameworks over prolonged periods in aqueous environments, even though it is known that many such materials are unstable in the presence of water (Burtch et al., 2014; Rego et al., 2021). Concerns about the stability LDH in an aqueous environment is less pressing than other inorganic materials due to widespread research into their use in biomedical applications, which have found LDH nanoparticles to have high stability at biological pH (Kuthati et al., 2015). However, there is a lack of knowledge regarding LDH stability as sorbent materials. There are two main implications of sorbent materials stability in water matrices: firstly, the possibility of secondary pollution to the water matrix reaching the environment; secondly, the chance of decreased sorption capacity of the sorbent material. Therefore, the relationships between the LDH sorbent material and ultrapure water and WWE matrix were investigated.

Comparing pXRD patterns of LDH following exposure to ultrapure water or WWE for 24 h showed no changes in the patterns, indicating the LDH structure is retained (Fig. 3c). This is to be expected, as dissolution of LDH is typically only observed under acidic conditions (Kotlar et al., 2020). At 30 min, near maximum SMX sorption, there are no additional reflections in the low 2θ range (4–30) of the pXRD pattern (Fig. 3c). This indicates sorption mechanisms in which intercalation of the pollutant into the interlayer region of the LDH do not take place. Intercalation of SMX into the interlayer spacing would be identifiable as an expansion of the interlayer region, resulting in additional (003) and (006) reflections in the pXRD pattern, as has been observed in the uptake of SMX by calcined-ZnAl-LDH (Mourid et al., 2019). Hence, SMX sorption to LDH is due to surface interactions with the LDH, such as favourable electrostatic interactions. No additional peaks can be seen in the FT-IR spectra, particularly in the $1370\text{--}1335 \text{ cm}^{-1}$ region where peaks corresponding to sulfonamide bonds in the SMX would be present (Maury et al., 1985). This is likely due to the low loadings of SMX present on the LDH ($< 0.157 \text{ mg/g}$), even at time points when maximum sorption is observed.

The concentration of NO_3^- , Mg and Al ions in ultrapure water were monitored following 24 h exposure to LDH, to understand if any leaching of LDH components into solution is taking place. Such information may provide insights into subsequent SMX sorption behaviour, as presence of ions into solution has been shown to impact SMX sorption onto LDH, as illustrated in the lack of SMX removal from WWE. An increase in $[\text{NO}_3^-]$ in ultrapure water was observed over 24 h, reaching a maximum concentration of $65.2 \pm 1.2 \text{ mg/g}$ of LDH (Fig. 3b), corresponding to a NO_3^- concentration of $131 \pm 2.4 \text{ mg/L}$. The increase in $[\text{NO}_3^-]$ is possibly due to anion exchange

between NO_3^- ions present in the interlayer of LDH with CO_3^{2-} present in solution. Free CO_3^{2-} anions are present in the water, occurring due to absorption from CO_2 (g) naturally present in the atmosphere (Al-Hindi and Azizi, 2018). Anion exchange is driven by the greater stability of CO_3^{2-} in the interlayer region of the LDH, due to the higher charged density of CO_3^{2-} compared to NO_3^- , as it is a well-known phenomenon interlayer anions will be replaced by preferred ions present in excess in solution (Braterman et al., 2005). This results in release of NO_3^- into solution and an LDH structure present with varying proportion of both anions present in the interlayer region. Release of NO_3^- from LDH structures has been widely reported in the context of using NO_3^- -LDH in agriculture, typically as slow-release fertilisers (Singha Roy et al., 2022). However, the impact that this might have on sorption performance is not discussed widely in the literature. Background ions can have a complex impact on sorption systems, hence it is important to understand how leached NO_3^- from LDH may be impacting sorption of SMX as well as other pollutants (Zhang et al., 2019).

To confirm NO_3^- in the water matrix was due to the interlayer characteristics of the LDH, an $\text{Mg}_2\text{Al-CO}_3$ -LDH was used for comparison. The same phenomenon was not observed in the case of MgAl-CO_3 -LDH analogue studied, with an equilibrium $[\text{NO}_3^-]$ of 12.9 ± 0.1 mg/g of LDH reached within 3 h (Fig. 3b). The presence of NO_3^- in the water, albeit at lower concentrations, is likely from the freely available NO_3^- still present in the LDH as a result of partially incomplete washing during synthesis of LDH, rather than anion exchange of interlayer anions. A similar solution pH was observed for both $\text{Mg}_2\text{Al-NO}_3$ -LDH and $\text{Mg}_2\text{Al-CO}_3$ -LDH, indicating solution properties were not driving the difference in the NO_3^- release observed (Fig. 3a).

Characteristically very small differences are seen between the FT-IR shifts for carbonate and nitrate ions within the interlayer region of LDHs (Hu et al., 2017). However, the 1358 cm^{-1} peak shifts to 1362 cm^{-1} for MgAl-NO_3 -LDH-synthesised and MgAl-NO_3 -LDH-ultrapure-24 h, indicating a possible change in the characterisation of the interlayer ions to a combination of NO_3^- and CO_3^{2-} , following possible anion exchange (Fig. 3d). Similarly, in MgAl-LDH-SMX-24 h shows a shift of 1362 cm^{-1} indicating partial anion exchange between NO_3^- and CO_3^{2-} in the case of exposure to SMX in ultrapure water. Such findings are in line with the changes in $[\text{NO}_3^-]$ in the ultrapure water (Fig. 3b). However, additional studies have reported that overlapping FT-IR shifts of CO_3^{2-} and NO_3^- in LDH samples are possible, hence the IR data presented cannot be considered conclusive (Bernard et al., 2022). Furthermore, for MgAl-CO_3 -LDH (not shown) as synthesised and after 24 h ultrapure water exposure, both show a peak due to the stretching vibration of carbonate, (νCO_3) at 1364 cm^{-1} , indicating no change in the characteristics of the interlayer anion in the LDH structure.

Leaching of Mg and Al from the metal-containing layers of the LDH was also determined. The Mg dissolution, at natural pH, for $\text{Mg}_2\text{Al-NO}_3$ -LDH was found to be < 1 wt%. Al dissolution was < 0.02 wt%, the lower value compared to Mg explained by the low solubility product (k_{sp}) of Al(OH)_3 , which is in the order of $\times 10^{-33}$ (Singh, 1974). Similar results have been reported for the dissolution of MgFe-LDH by Kotlar et al. (2022). The molar concentrations of leached metals are found to be lower than that of leached NO_3^- after 24 h (Table 1), and considering the expected ratio of Mg to NO_3^- within the LDH structure (2:1), the concentration of NO_3^- in solution cannot be fully explained by LDH dissolution alone. Therefore, it is suggested that NO_3^- release is due to a combination of anion exchange alongside partial dissolution of the $\text{Mg}_2\text{Al-NO}_3$ -LDH structure causing release of interlayer ions. Furthermore, there is the added complexity of quantifying exact NO_3^- concentration in the water matrix following exposure to the LDH, due to the possibility of direct sorption of NO_3^- onto the surface of the LDH (Halajnia et al., 2013; Tezuka et al., 2004; Xue et al., 2016).

3.5. Role of background anions on SMX sorption to LDH

The role of NO_3^- in the water matrix as a disrupter for SMX-LDH interactions, which results in desorption of the SMX from LDH back into the water matrix was considered (Fig. 4a). The SMX behaviour was found to mirror the behaviour of SMX in ultrapure water in two different $[\text{NO}_3^-]$ backgrounds (50 mg/L and 250 mg/L), with an initial sorption of SMX onto the LDH followed by desorption of SMX back into solution. This resulted in no equilibrium uptake of SMX after 24 h. The maximum SMX removal percentage was dependent on background $[\text{NO}_3^-]$, decreasing from $34.8 \pm 2.05\%$ in ultrapure water to $8.8 \pm 0.32\%$ in the presence of 250 mg/L NO_3^- . The sorption of pollutants to sorbent materials is typically negatively impacted by the background ions in solution, through both the obstruction of electrostatic interactions and sorbing preferentially to sorption sites, with increasing salt concentration (Crini and Badot, 2008). Background ions may also alter speciation of the pollutant, through increasing the degree of pollutant dissociation, boosting the sorption capacity to the sorbent (Crini and Badot, 2008). It has been previously reported that LDH can adsorb NO_3^- from water (Halajnia et al., 2013; Tezuka et al., 2004; Xue et al., 2016). Therefore, NO_3^- is likely competing with SMX for the sorption sites on the LDH surface, resulting in a decrease in available sorption sites for the SMX. The competition is further validation for surface interactions to be the predominant driving factor behind the initial decrease in solution SMX concentration.

Due to the concurrent nature of the sorption and desorption processes of SMX onto LDH it is not possible to apply traditional sorption kinetic models to the processes. However, the kinetics of sorption appear to be impacted by the presence of background $[\text{NO}_3^-]$, with the time taken to reach the maximum removal capacity increasing from 10 min to 30 min as the $[\text{NO}_3^-]$ increases from ultrapure water to 250 mg/L. Such decrease in rate of sorption with increased presence of background ions has been reported for other systems, including for the protein Cry_1Ab onto SiO_2 due to the shielding of favourable electrostatic interactions (Zhang et al., 2019).

Table 1

Molar concentrations of LDH components in solution per g of LDH (N = 3 SD errors shown in brackets). Reaction conditions: $[\text{LDH}] = 2\text{ g/L}$, $T = 20\text{ }^\circ\text{C}$, continuous stirring.

LDH	[Al] $\mu\text{M/g LDH}$	[Mg] $\mu\text{M/g LDH}$	$[\text{NO}_3^-]$ mM/g LDH
$\text{Mg}_2\text{Al-NO}_3$	6.27 (± 1.15)	278.18 (± 3.53)	1.05 (± 0.02)
$\text{Mg}_2\text{Al-CO}_3$	0.23 (± 0.18)	272.70 (± 22.11)	0.21 (± 0.00)

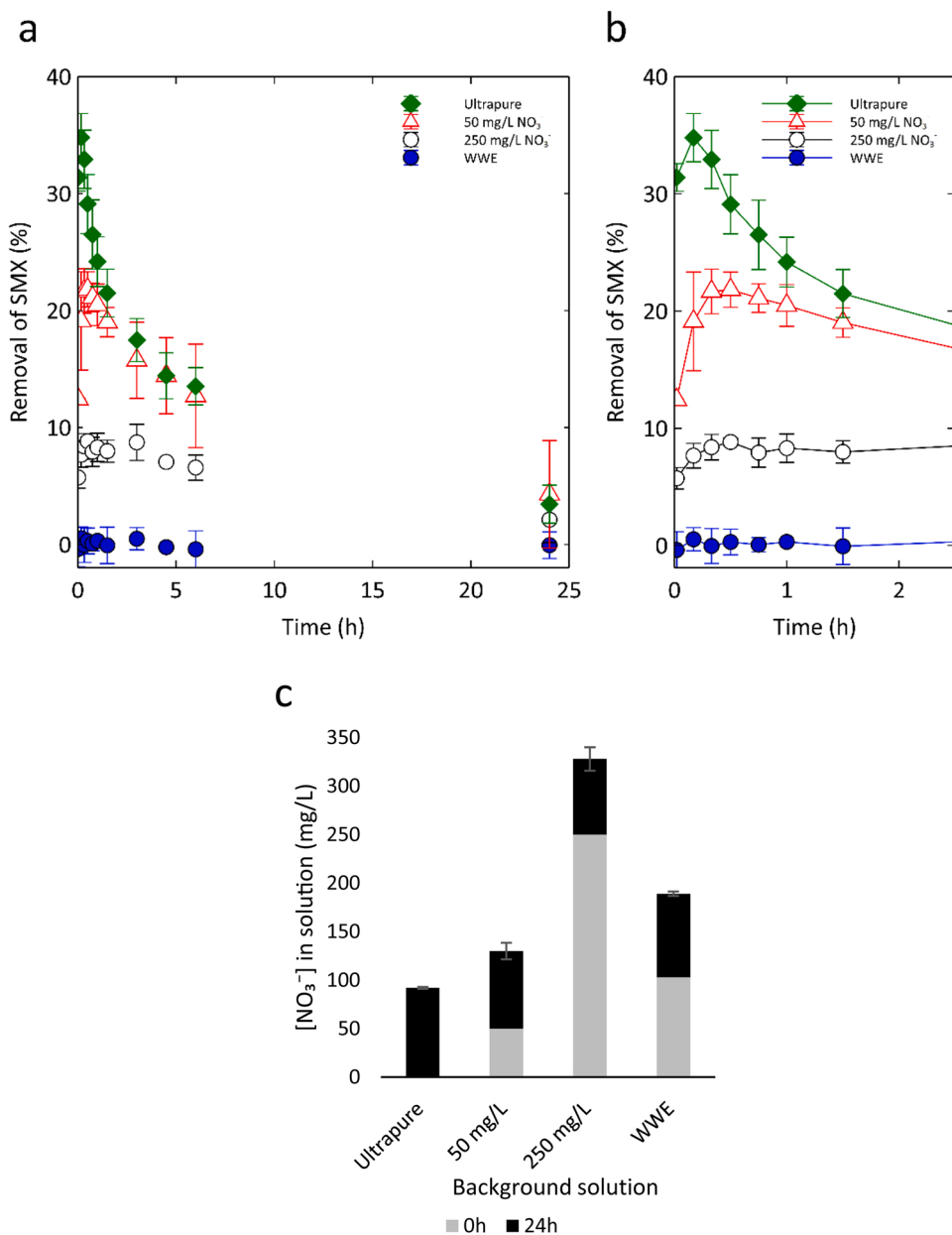


Fig. 4. (a) SMX removal percentage with time 0–24 h and (b) 0–2.5 h for differing adsorbent media. The removal percentage of SMX over time is shown for ultrapure water (green diamonds), 50 mg/L NO₃ (aq) (red triangles), 250 mg/L NO₃ (aq) (open black circles), and wastewater effluent (blue circles). Reaction conditions: [SMX] = 100 µg/L, [LDH] = 0.80 g/L, T = 20 °C, continuous stirring. Error bars calculated from N = 3 samples, including from WWE collected on one day. Lines are shown to guide the eye only (c) Change in [NO₃⁻] in solution before and after SMX removal experiments with varying sorption solutions, between t = 0 h and t = 24 h. Reaction conditions: [SMX] = 100 µg/L, [LDH] = 0.80 g/L, T = 20 °C, continuous stirring.

3.6. Proposed mechanism explaining SMX sorption behaviour

Desorption of SMX from the LDH to ultrapure water can be mapped against the increasing [NO₃⁻] released from the LDH into solution (Fig. 4b). The anion exchange between LDH interlayer NO₃⁻ and CO₃²⁻ present in the solution can infer a pseudo-elevated nitrate concentration at the boundary layer at the LDH surface. Rather than diffusing through the boundary layer to the bulk solution, some of the leached NO₃⁻ is able to interact with the LDH surface thereby displacing the weak SMX-LDH sorption interactions. Weak interactions between LDH and SMX are expected, characterised by the low soil sorption coefficients, K_d, recorded for sulfonamide antibiotics (Harrower et al., 2021). With an increase between released nitrate concentration (up to 100 mg/L) compared to initial SMX concentration (100 µg/L) in the water matrix, it can be envisioned that only a small proportion of the released NO₃⁻ is required to fully

displace the adsorbed SMX. The irreversible sorption of NO_3^- to the LDH surface blocks any subsequent resorption of the SMX in solution. The speculated mechanism is shown in Fig. 5. Whilst such behaviour of released NO_3^- disrupting pollutant-LDH interactions is not overtly discussed in the literature, there is a precedent for NO_3^- disrupting the interactions between anionic pollutants and MgAl-LDH in sorbent material regeneration experiments (Shamsayei et al., 2018).

As previously discussed, studies by Wang et al. (2022) and Lv et al. (2021) have illustrated that SMX sorption can be unexpectedly reversible, and therefore it is not unprecedented that the SMX interactions are weak enough to be interrupted. Furthermore, there are examples of SMX desorption from clays and soils, which may be analogous to LDH sorption (Franklin et al., 2022). Sulfamethoxazole has been shown to succumb to desorption through competition for sorption site with natural organic matter present in wastewater, and this is found to be more prominent for SMX than observed for a second antibiotic, Ciprofloxacin, which has a greater binding affinity to the soils (Carrillo et al., 2016). Additionally, π - π interactions have been shown to be key contributors in SMX sorption, therefore the lack of aromatic functionality on LDH surfaces may contribute to weak SMX sorption (Lan et al., 2016; Lv et al., 2021).

3.7. SMX sorption behaviour onto alternative LDH

To aid in the understanding of SMX sorption behaviour in the presence of $\text{Mg}_2\text{Al-NO}_3$ -LDH, further LDHs (Supplementary Information, Figure S10) were evaluated for SMX sorption from ultrapure water (Fig. 6). The LDHs were selected to understand if changing

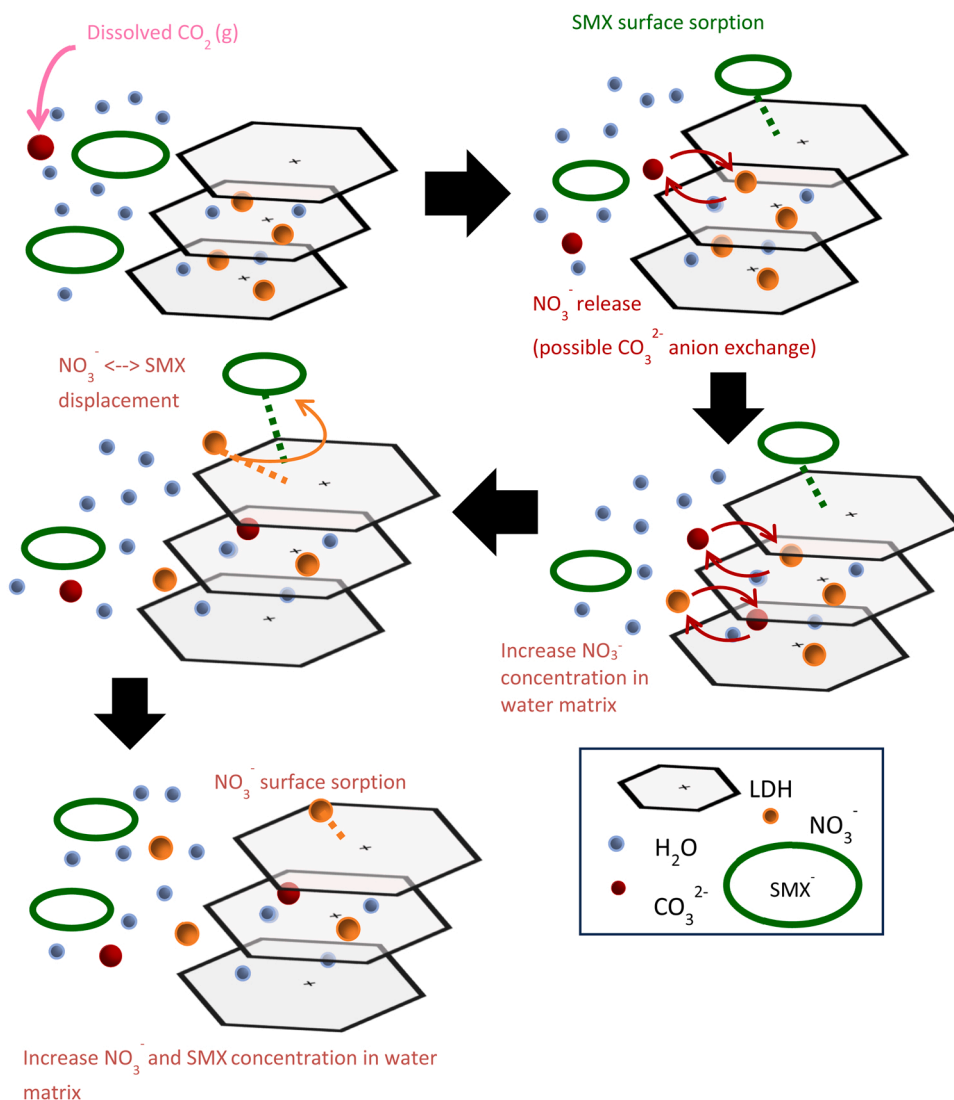


Fig. 5. Illustration of the proposed mechanism of SMX sorption and displacement on $\text{Mg}_2\text{Al-NO}_3$ -LDH sample in ultrapure water-based matrices. In the case of wastewater effluent, the large number of components present can fully outcompete the initial sorption of SMX resulting in no sorption/release mechanism observed.

interlayer anion, M(II):M(III) ratios and the trivalent metal impact the SMX sorption behaviour.

The LDH M(II):M(III) ratio influences SMX sorption, with the maximum removal percentage decreased from $34.8 \pm 2.05\%$ to $16.8 \pm 1.37\%$ in the presence of $\text{Mg}_2\text{Al-NO}_3\text{-LDH}$ and $\text{Mg}_4\text{Al-NO}_3\text{-LDH}$ respectively. Decreasing the proportion of Al in the $\text{Mg}_4\text{Al-NO}_3\text{-LDH}$ results in the lower overall positive charge density of the LDH layers, which is a contributing factor in decreased sorption of anionic pollutants on to LDH surface (Morimoto et al., 2011). Furthermore, the decrease in maximum removal percentage with decreasing proportion of Al contributes to the understanding that the sorption of SMX onto LDH is largely due to surface interactions rather than anion exchange. Additionally, SMX sorption is again found to be reversible in the case of $\text{Mg}_4\text{Al-NO}_3\text{-LDH}$. This is to be expected, as interlayer NO_3^- release allowing for displacement of the surface sorbed SMX takes place, as in the case of $\text{Mg}_2\text{Al-NO}_3\text{-LDH}$ (Supplementary Information, Figure S11).

Alternative behaviour is seen for $\text{Mg}_4\text{Fe-NO}_3\text{-LDH}$ and $\text{Mg}_2\text{Al-CO}_3\text{-LDH}$ which do not exhibit SMX sorption/desorption, with a maximum removal percentage of $1.97 \pm 1.17\%$ and $4.32 \pm 2.27\%$ respectively. The lack of SMX sorption on $\text{Mg}_4\text{Fe-NO}_3\text{-LDH}$ can possibly be explained by the lower zeta potential of the sample, $+17.6$ mV compared to $+32.0$ mV for $\text{Mg}_2\text{Al-NO}_3\text{-LDH-bulk}$ (Supplementary Information, Table S5), which results in increased LDH particle aggregation. The difference in sorption of doxycycline from ultrapure water on to MgAl-LDH (98.8 mg/g) and MgFe-LDH (12.3 mg/g) has been explained through similar differences in zeta potential, 26.6 and -17.8 mV respectively (Moaty et al., 2019).

The sorption behaviour of SMX in the presence of $\text{Mg}_2\text{Al-CO}_3\text{-LDH}$ is less comparable to the initial SMX interactions with $\text{NO}_3\text{-LDH}$. The lack of SMX sorption to the $\text{Mg}_2\text{Al-CO}_3\text{-LDH}$ can be explained through the difference in pH_{PZC} , being 8.94 and lower than all $\text{NO}_3\text{-LDH}$ examples in this work (Supplementary Information, Table S5). As a result, at the solution pH of 8.5 , the $\text{Mg}_2\text{Al-CO}_3\text{-LDH}$ will have a net surface charge closer to neutral than the other LDHs studied. This will weaken further the chance of favourable electrostatic interactions between the LDH surface and anionic SMX, resulting in very low uptake of SMX. For $\text{Mg}_2\text{Al-CO}_3\text{-LDH}$, as CO_3^{2-} is the interlayer anion, in place of NO_3^- , the leached $[\text{NO}_3^-]$ is much lower than the $\text{Mg}_2\text{Al-NO}_3\text{-LDH}$ (Fig. 3b). Therefore, the initial SMX sorption/distribution mechanism caused by released NO_3^- would not be expected to take place to the same extent. It would be valuable to understand the relationship between SMX sorption/desorption and LDH interlayer anion in more detail, as sorption performance has been found to vary between LDH structures with different interlayer anions (Johnston et al., 2021). For example, the sorption behaviour of SMX onto LDH structures with Cl^- and SO_4^{2-} as interlayer anions, in addition to CO_3^{2-} and NO_3^- , should be explored in future work.

There are limited studies which consider the removal of sulfonamide antibiotics using LDH based sorbent materials, hence the overall findings of this study (i.e. no equilibrium uptake of SMX) are not unexpected. However, there are examples in the literature of alternative sorbent materials which have displayed successful sorption of SMX from different water matrices, including from WWE, albeit at lower sorption capacities than in deionised water (Table 2). Hence it is possible LDH materials could be modified, such as included in composite materials, to result in successful sorbent materials for the removal of SMX.

4. Conclusions

Layered double hydroxides can be synthesised through a scalable continuous synthesis technique, making them ideal candidates for commercial sorbent materials (Clark et al., 2019). Furthermore, due to their physiochemical properties LDH are considered suitable

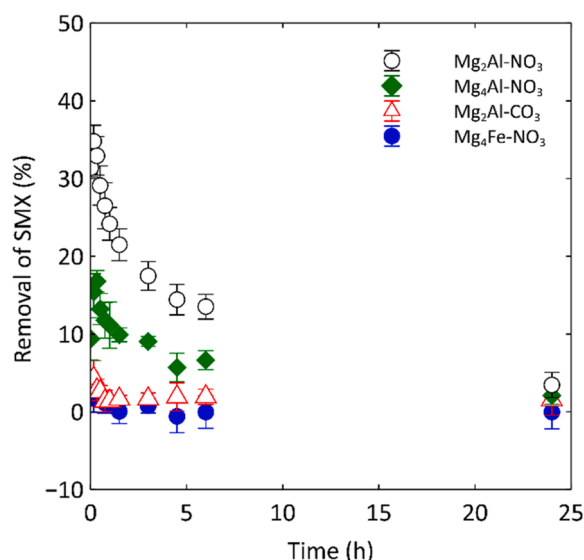


Fig. 6. Removal percentage of SMX from ultrapure water in the presence of $\text{Mg}_2\text{Al-NO}_3\text{-LDH}$ (black outline circles), $\text{Mg}_4\text{Al-NO}_3\text{-LDH}$ (green diamonds), $\text{Mg}_2\text{Al-CO}_3\text{-LDH}$ (red outline triangle), and $\text{Mg}_4\text{Fe-NO}_3\text{-LDH}$ (blue circles), between 0 - 24 h. Reaction conditions: $[\text{SMX}] = 100 \mu\text{g/L}$, $[\text{LDH}] = 0.80 \text{ g/L}$, $T = 20 \text{ }^\circ\text{C}$, continuous stirring.

Table 2

Comparison of maximum equilibrium sorption capacity of different sorbent materials for the removal of sulfamethoxazole (SMX) from various water matrices. ND – not determined for this work due to sorption/desorption matrix.

Sorbent material	q_{\max} (mg/g)	Water matrix	Reference
Mg ₂ Al-NO ₃ -LDH (via continuous synthesis)	ND	Laboratory-grade water	This work
	ND	Municipal wastewater effluent	
MgAl-CO ₃ -LDH (via a co-precipitation synthesis)	0.37	Deionised water	(Li et al., 2019)
Iron-loaded sludge biochar	80.2	Deionised water	(Hu et al., 2023)
Ball-milled biochar	100.3	Deionised water	(Huang et al., 2020)
	25.7	Municipal wastewater effluent	
Ex-situ magnetic activated carbon	167	Ultrapure water	(Pereira et al., 2023)
	37	Municipal wastewater effluent	

sorbent materials for removing anionic organic pollutants including pharmaceuticals, from water matrices. However, this study shows that Mg₂Al-NO₃-LDH does not effectively remove SMX from either ultrapure water or wastewater effluent over 24 h. Pollutant sorption behaviour differs depending on the water matrix, hence the complexity of the water matrix must be considered early in the development stages of new LDH sorbent materials. This will ensure the correct understanding of applicability of LDH sorbent materials for any possibility of future widespread applications, and movement up Technology Readiness Levels. Likewise, future work should also consider the regeneration and the reuse of the LDH through multiple sorption cycles, to demonstrate suitability for widespread wastewater treatment applications.

This study reveals LDH materials are altering the water matrix during their application in sorption processes. Through both partial dissolution of the LDH structure and anion exchange of aqueous CO₃²⁻, release of the interlayer anion from the LDH results in the increase in [NO₃⁻] in the background solution. As SMX sorption is influenced by the water matrix characteristics, it is suggested that [NO₃⁻] release is driving irreversible release of initial sorbed SMX from LDH surface. Furthermore, increase in concentration of NO₃⁻ from the LDH in the water may have wider implications if MgAl-NO₃-LDH is to be used as a sorbent material in an advanced wastewater treatment technology. Depending on specific wastewater treatment site characteristics, the discharge of wastewater effluent will have regulatory total nitrogen concentration limits, of which NO₃⁻ ions are included in the count. Release of additional nitrogen during advanced treatment could result in an increase above regulatory levels (<10 mg/L for >100,000 PE) and could further result in detrimental environmental impacts through eutrophication. In addition, if concentrations of leached metals (in this case Mg or Al) from the LDH during use as a sorbent material were found to be above certain limits, permits would be required for the discharge of the wastewater effluent from the treatment site. This work highlights the complexity of sorption processes, illustrating the potential for interactions between both the sorbent material and water matrix, consequently impacting expected pollutant sorption behaviour.

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CRedit authorship contribution statement

Johnston Amy-Louise: Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft. **Williams Orla:** Supervision. **Lester Edward:** Conceptualization, Methodology, Resources, Supervision, Writing – review & editing. **Gomes Rachel Louise:** Conceptualization, Funding acquisition, Methodology, Project administration, Resources, Supervision, Validation, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.eti.2023.103490](https://doi.org/10.1016/j.eti.2023.103490).

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