Chemosphere 367 (2024) 143546

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Interactions between antibiotic removal, water matrix characteristics and layered double hydroxide sorbent material

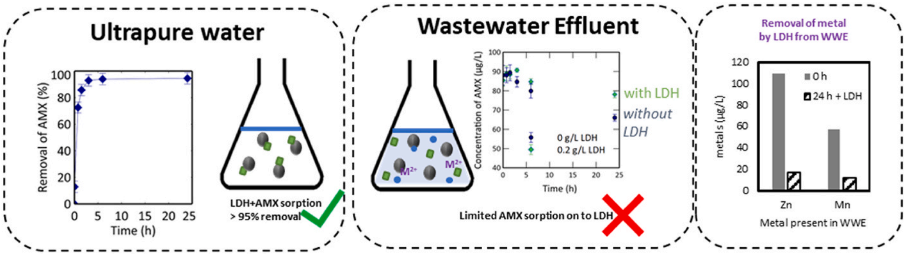
Amy-Louise Johnston [a,b], Edward Lester [b], Orla Williams [b], Rachel L. Gomes [a,*]

[a] *Food Water Waste Research Group, Faculty of Engineering, University of Nottingham, Nottingham, NG7 2RD, UK*
[b] *Advanced Materials Research Group, Faculty of Engineering, University of Nottingham, Nottingham, NG7 2R, UK*

HIGHLIGHTS

- Amoxicillin removed by 95% from laboratory-grade water by MgAl–NO_3-LDH.
- Spontaneous and endothermic sorption of amoxicillin from laboratory-grade water.
- Reduced removal of amoxicillin observed from wastewater effluent by MgAl–NO_3-LDH.
- Decrease in amoxicillin concentration in wastewater effluent without LDH present.
- Metal pollutants in wastewater effluent are removed in the presence of MgAl–NO_3-LDH.

GRAPHICAL ABSTRACT



ARTICLE INFO

Handling editor: Y Yeomin Yoon

Keywords:
LDH
Wastewater treatment
Adsorption
Competition
Pharmaceuticals
Metals

ABSTRACT

Sorption by layered double hydroxides (LDH) is gaining substantial interest for remediating emerging contaminants, including pharmaceuticals from wastewaters. Findings from a sorbent material performing successfully in lab-based studies using non-environmental (laboratory-sourced) water cannot be assumed to translate to equal performance under environmental downstream applications. However, studies evaluating sorbent material performance for removal of pollutants and understanding material interactions with environmental waters are limited. This study evaluates the removal of the antibiotic amoxicillin (AMX) using a Mg_2Al–NO_3-LDH sorbent material from laboratory-grade water and wastewater effluent (WWE). AMX is successfully removed (94.53 ± 4.30 % within 24 h) in laboratory-grade water (under batch sorption conditions: 100 μg/L AMX, 0.2 g/L LDH, 20 °C). The comparison of LDH removal performance in laboratory grade and WWE shows a decreased maximum removal of AMX in WWE (13.39 ± 5.53 %). A lower final AMX concentration is observed in the WWE without the presence of LDH, compared to the 'removal' experiments in WWE with the presence of LDH, indicating a contribution of non-sorption removal pathways of AMX. This is proposed to be due to the difference in metal concentrations in the WWE with and without LDH present. The presence of LDH is found to decrease concentrations of metal pollutants in WWE, such as Zn concentration decreasing by 85 % over 24 h, changing water characteristics. Overall, this paper reports that an LDH performs differently in laboratory-sourced water and a wastewater effluent. This provides evidence that sorbent material performance needs to be evaluated in complex water matrices to ensure that it is representative of how a sorbent material will perform in an environmental application, which is the end goal of developing such technologies. Finally, good practice recommendations are

---

[*] Corresponding author.
E-mail address: rachel.gomes@nottingham.ac.uk (R.L. Gomes).

https://doi.org/10.1016/j.chemosphere.2024.143546
Received 26 July 2024; Received in revised form 11 October 2024; Accepted 12 October 2024

provided for future lab-scale sorption experiments evaluating the performance of any new sorbent materials for water treatment applications.

1. Introduction

Amoxicillin (AMX) is a β-lactam antibiotic included on the World Health Organisation list of essential medicines, used globally in human and veterinary medicine (World Health Organization, 2023). It is the most commonly used antibiotic in over two-thirds of European counties, and consumption of β-lactam antibiotics grew by 35 % in the 10 years prior to 2010 (Litskas et al., 2018). As a result of anthropogenic activities, antibiotics, including AMX are entering the water environment. Antibiotics are included in a class of pollutants known as emerging contaminants, and are present in nearly all environmental waters globally, ranging from surface water through to pharmaceutical manufacturing wastewater effluent (aus der Beek et al., 2016; Larsson et al., 2007). The ubiquitous presence of antibiotics in the environment is causing ecotoxicity, including health impacts such as endocrine disrupting effects (Wilkinson et al., 2016). Additionally, antibiotics in environmental waters are a driver for the spread of antimicrobial resistance, which is already considered to be a leading cause of death globally (Trust, 2018; Chow et al., 2021; Murray et al., 2022). With the rise in use of antibiotics, their removal from environmental waters is crucial to reduce the negative impacts resulting from water pollution and contribute to the success of the United Nations Sustainable Development Goal 6: *Clean water and sanitation* (UN General Assembly, 2015).

Similar to other emerging contaminants, AMX cannot be adequately removed during the wastewater treatment process (WWTP), with AMX concentration in wastewater effluent (WWE) found to be up to 622 ng/L to 1600 ng/L, depending on geography and/or treatment process (Kasprzyk-Hordern et al., 2008; Kairigo et al., 2020). Furthermore, antibiotic removal through WWTPs is reported to be <10% for many pharmaceuticals, as WWTPs were never designed to remove such pollutants (Patel et al., 2019). Further, legislation within the European Union is progressing towards a mandatory requirement for wastewater treatment plants over a certain size to have advance water treatment for removal of emerging contaminants, with associated additional costs being contributed to through extended producer responsibility. (Council of the EU and Press Release) This has motivated the development of advanced water treatment technologies, in which sorption-based technologies are advantageous due to their low cost, simplicity of design, and support to circular economy thinking (e.g. pollutants to products) (Dotto and McKay, 2020). Various sorbent materials including, but not limited to, activated carbons from multiple feedstocks, (magnetic)-nanoparticles, metal organic frameworks (MOFs) such as MIL-53(Al), and clays such as organobentonite have been applied for removal of amoxicillin, with their performance extensively reviewed (Georgin et al., 2023).

Layered double hydroxides (LDHs) are emerging as excellent sorption materials for the removal of organic pollutants (Johnston et al., 2021; Yang et al., 2016). LDH, also known as anionic clays, consist of a layered structure with the generic chemical structure $[M^{2+}_{1\text{-}x}M^{3+}_{x}\,(OH)_2]\,(A^{n-})_{x/n}\bullet mH_2O$, allowing for the inclusion of multiple different metals and interlayer anions (Braterman et al., 2005). The physicochemical properties of LDH include high surface areas (Chen et al., 2018), and a structure which gives rise to the possibility of various sorption mechanisms to occur, including anion exchange (Chen et al., 2019) and electrostatic interactions with the positively charged surface (El Hassani et al., 2017). Further, there is limited concern around the stability of LDH-based sorbent materials as the secondary pollution of waters with metals during exposure of LDH to water is limited (Goh and Lim, 2010), which is not always the case with alternative inorganic sorbent materials such as MOFs (Burtch et al., 2014).

Knowledge concerning utilising LDHs for removing antibiotic pharmaceuticals from water is limited, especially when compared to other common pollutants such as dyes or oxyanions (Johnston et al., 2021, 2024; Yang et al., 2016; Goh et al., 2008; Nava-Andrade et al., 2021). Whilst there are studies evaluating AMX removal from water using LDH-based sorbent materials, each of the studies consider the removal of AMX at starting concentrations ≥20 mg/L, much greater than environmentally-relevant concentrations (Elhaci et al., 2020; Liu et al., 2022; Yang et al., 2020). More generally, studies evaluating the performance of LDH sorbent materials with starting concentrations of antibiotics at environmentally-relevant concentrations (μg/L rather than ≥ mg/L) are limited in the literature (da Silva et al., 2021). Further, each of the studies only consider AMX removal from laboratory-grade water, rather than more complex environmental waters with the presence of competing pollutants (Elhaci et al., 2020; Liu et al., 2022; Yang et al., 2020). Successful investigations into the removal of antibiotics from complex environmental waters using LDH sorbent materials have not been previously reported in the literature. Further, whilst there are examples of LDH removing metals from complex industrial waters (Cardinale et al., 2020; Álvarez-Ayuso and Nugteren, 2005; Zhang et al., 2012), only one study is known for the removal of an organic pollutant from complex environmental waters using LDH-based sorbent materials, removal of a dye *Reactive Red* from river water, municipal wastewater influent and effluent (Munonde et al., 2022). Additionally, removal of amoxicillin from complex water matrices by other sorbent materials are also little explored, especially compared to other pharmaceutical pollutants such as tetracyclines or naproxen (Georgin et al., 2023). Studies which consider environmental relevance, including treating waters with pollutants at environmental concentrations and the presence of multiple pollutants, are crucial. Such experiments allow for the understanding of competition and interactions between different pollutants and their impact on sorption; selectivity of sorbent materials for a particular pollutant/s of interest; variation in sorption kinetics and removal (sorption) capacities under these conditions when compared to calculated maximum sorption capacities (Dotto and McKay, 2020). Such research gaps limit the understanding the suitability of LDHs for antibiotic removal and translation to more developed technology readiness levels.

This study aims to address this gap in knowledge on how LDH sorption performs on environmental wastewater compared to idealised laboratory-grade water. Therefore, the objectives of this paper were to, for the first time:

i. Evaluate the performance of MgAl–NO_3-LDH, synthesised through a scalable continuous method, for the removal of AMX from laboratory-grade and environmental water matrices (wastewater effluent), allowing for a deeper understanding of the impact of the water matrix on LDH sorption performance.
ii. Investigate possible reasons for varying sorption performance between laboratory-grade and environmental water matrices (wastewater effluent) through the interactions between the LDH and wastewater effluent. This work further aims to expose the possible relationship with both reduction in AMX sorption and consequences on AMX degradation pathways between different water matrices.

2. Materials and methods

2.1. Chemicals and reagents

Methanol (MeOH) and acetonitrile (ACN) used for chromatography purposes were liquid chromatography mass spectrometry (LCMS)-grade, purchased from ThermoFisher (Loughborough, UK). Antibiotic stock preparation also used MeOH of HPLC grade. Laboratory-grade water (18.2 mΩ) was used for all experiments, unless otherwise stated. For synthesising the LDH material, magnesium nitrate hexahydrate (98+ %) was also purchased from Fisher Scientific. Amoxicillin (90+ %), formic acid (CHOOH), sodium nitrate (99+ %), and sodium hydroxide (97+ %) were all purchased from Sigma Aldrich (Devon, UK). Aluminium nitrate hexahydrate (98+ %) was purchased from Alfa Aesar (MA, USA). All chemicals were reagent grade and used as received. The synthesis and full characterisation of the $Mg_2Al–NO_3$-LDH sorbent material used throughout this work has been described elsewhere (Johnston et al., 2024). The synthesis utilised a bench-scale continuous hydrothermal flow reactor (Williams et al., 2019), with the product oven dried, crushed, and characterised, before being applied as a powdered sorbent material. The continuous hydrothermal flow reactor is a sustainable and scalable synthesis technology, suitable for manufacture of LDH for any future widespread usage of LDH as a sorbent material (Clark et al., 2019). Rational for selection of a Mg and Al containing LDH are:

- synthesised using the continuous hydrothermal flow reactor at relatively ambient conditions (<100 °C) (Johnston et al., 2024).
- Al and Mg are not considered to have a serious threat of future supply; hence they have better scope for widespread application than LDH based sorbent material containing metals such as Zn considered to have a serious threat to future availability. (European Chemical Society and Elem)
- whilst full assessment of the hazards of LDHs have not yet been conducted, the associated Mg and Al hydroxides are not considered to be hazardous substances according to regulation (EC) No 1272/2008.
- to avoid use of heavy metals within the LDH averting possible leaching of heavy metals from materials during application which would have more significant environmental implication then leaching of an equal quantity of Mg and Al, due to differences in inherent toxicity.

2.2. *Batch sorption experiments of AMX from laboratory-grade water*

Unless stated otherwise, 0.05 g of $Mg_2Al–NO_3$-LDH sorbent material was dispersed into 250 mL water pre-spiked with 100 μg/L AMX solution at 20 °C. Solutions were continuously stirred in a temperature-controlled incubator for 24 h. At set time points, 1.5 mL of solution was removed from the reaction vessel and centrifuged at 13,400 rpm for 3 min to remove the solid LDH material. An aliquot of the supernatant (1 mL) was then removed and stored at 4 °C until analysis (carried out within ≤24 h) by LC-MS/MS (supplementary information). Glassware was either amber or foil covered to avoid photodegradation of AMX. All AMX solutions were made up on a weekly basis in laboratory-grade water, diluted from an initial 1 g/L stock in MeOH.

To understand how experimental conditions impacted sorption performance, experimental conditions were altered including temperature (5–30 °C), AMX concentration (10–500 μg/L), and LDH mass (0.2–0.64 g/L). The natural pH of the solution was used as is throughout all experiments and monitored during sorption experiments at pre-defined time points. pH dependent experiments were not conducted due to the known buffering properties of LDH (Yang et al., 2016; Liu et al., 2022). Control experiments were carried out alongside all removal experiments to account for any abiotic or biotic degradation of AMX and ensure quantifying AMX removal was due to LDH sorption alone.

The sorption performance of the LDH for the removal of AMX form the liquid phase was calculated as the sorption capacity and the removal percentage. Sorption capacity (q_t) (mg/g) of the LDH for the AMX removal from water was calculated using the following equation:

$$q_t = \frac{(C_0 - C_t) \times V}{m} \qquad \text{Equation 1}$$

Further, the removal percentage (*%R*) is calculated as follows:

$$\%R = \frac{C_0 - C_t}{C_0} \times 100 \qquad \text{Equation 2}$$

where C_0 is the initial AMX concentration in solution (mg/L) and C_t is the AMX concentration (mg/L) in solution at a given time (t). V is the volume of the solution (L) and m the mass of LDH used (g). Unless otherwise stated, analysis was carried out in triplicate, with SD errors shown. The concentration of AMX in solution was quantified using liquid chromatography tandem mass spectrometry (LC-MS/MS), details of which are included in the supplementary information.

2.3. *Amoxicillin removal from wastewater effluent*

Sorption experiments were conducted with AMX-doped WWE. The WWE was sampled from Stoke Bardolph WWTP (Nottinghamshire, UK) between July 2022 to May 2023. The WWTP serves a population equivalent of ~620,000, utilising advanced activated sludge treatment. Prior to characterisation and utilisation in AMX removal experiments, the WWE was filtered through 1.2 μm pore size micro glass fibre filter paper (Fisher Scientific, Loughborough, UK) to remove suspended solids and used within 4 h of sampling. The batch sorption set-up outlined in Section 2.2 was used to understand the removal of AMX from WWE, with filtered-WWE used in place of laboratory grade water, and all other experimental conditions kept constant.

2.4. *Characterisation of wastewater effluent*

The WWE was characterised prior to use in sorption experiments and characteristics are summarised in Tables S1 and S2. Total suspended solids (TSS) were measured photometrically using DR 2800 Spectrophotometer (Hach, Manchester, UK). Chemical Oxygen Demand (COD) was determined photometrically by cuvette test (LCK500, ISO 15705, 0–150 mg/L O_2; Hach, Manchester, UK) using a DR 2800 Spectrophotometer, as per Hach working procedure. Conductivity was measured using a FiveGo Portable F3 Conductivity Meter (Mettler Toledo, USA). Dissolved Oxygen (DO) was measured using a HQ40D DO probe (Hach, Manchester, UK). The concentration of trace metals in WWE were quantified using inductively coupled plasma mass spectrometry (ICP-MS, Section 2.5).

2.5. *Metal concentration in wastewater*

To understand the impact and any interdependencies between the LDH sorbent material and metal pollutants inherently present in WWE, the metal concentrations in solution following batch sorption experiments of AMX were quantified using ICP-MS. Control experiments, WWE with 0.2 g/L LDH, WWE with 100 μg/L AMX, and WWE only, were conducted alongside the removal experiments of WWE doped with 100 μg/L AMX and 0.2 g/L LDH (as per Section 2.3). In each case, 50 mL of experimental solution was removed after 24 h, and centrifuged at 4000 rpm for 20 min. Three 10 mL aliquots of the supernatant were then passed through a 0.45 μm polyethersulfone (PES) syringe filter (Camlabs, UK), acidified to a 2% v/v nitric acid concentration and stored at 4 °C prior to analysis. The multi-element analysis of solutions for metal quantification was undertaken by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Thermo-Fisher Scientific iCAP-Q; Thermo Fisher Scientific, Germany), details included in supplementary information.

3. Results and discussion

3.1. *AMX sorption of AMX from laboratory-grade water*

3.1.1. *AMX removal and sorption capacity*

The $Mg_2Al–NO_3$-LDH sorbent material was found to remove ≥95% of

AMX from laboratory-grade water, reaching an equilibrium removal withing 3 h (Fig. 1). In subsequent experiments, standard reaction conditions were kept consistent, 100 μg/L AMX, 0.2 g/L LDH, 20 °C, under continuous stirring in dark conditions, with only single parameters changed in each experiment to understand the impact of the changing experimental condition. For all experimental conditions it was found that an equilibrium removal capacity was achieved within 24 h, and hence this timeframe was used for determining sorption kinetics of all experiments using laboratory-grade water as the water matrix.

The AMX removal behaviour is explained due to the presence of favourable electrostatic interactions between the AMX and the surface of the LDH sorbent material. AMX (Fig. S1) has pKa values of 2.69, 7.49, and 9.63 (Homem et al., 2010). The AMX structure will be a zwitterion with solution pH values between 2.69 and 7.49, and an anion when the solution pH is > 7.5, due to the protonation and deprotonation of the amine and the carboxylic acid functional groups. The pH_{PZC} of $Mg_2Al–NO_3$- LDH is calculated to be 10.04, in agreement to previously reported values, and therefore the LDH surface will be positively charged (Goh et al., 2008; Johnston et al., 2024). The pH of point zero charge (pHPZC) value for the LDH were determined using a pH drift method, as previously reported (Johnston et al., 2024; Ateia et al., 2020).

On introduction of 0.2 g/L $Mg_2Al–NO_3$-LDH to laboratory-grade water, the pH increased from 5.5 reaching an equilibrium value of 7.9, in agreement with previously reported pH buffering behaviour of LDHs (Fig. 2e.) (Singha Roy et al., 2023) The natural solution pH was used throughout for all experiments. At natural solution pH, AMX is present in anionic form, and the LDH surface positively charged, demonstrating favourable electrostatic interactions between pollutant and sorbent material. Additionally, there may be some contribution of sorption via anion exchange between the interlayer anion (NO_3^-) and the anionic AMX. To be able to understand the exact sorption mechanism in more detailed, future research should consider the change to the LDH structure following sorption utilising standard materials characterisation techniques.

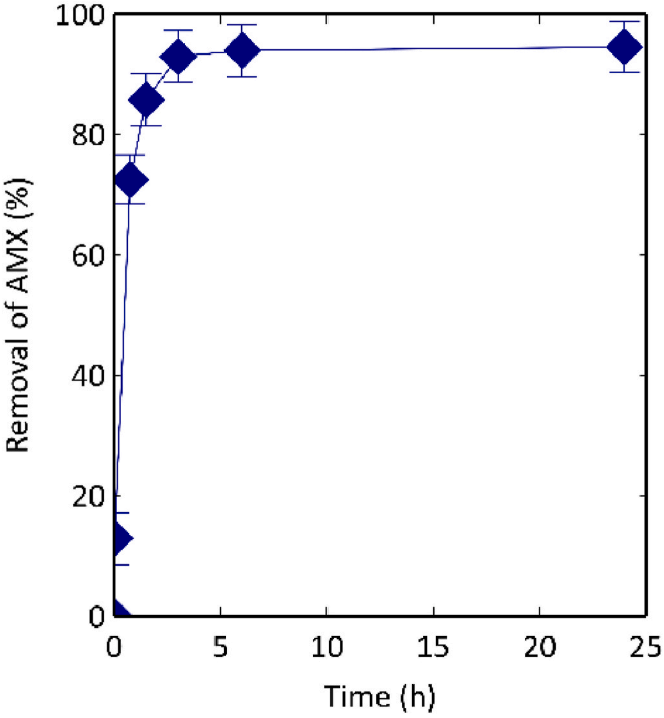


Fig. 1. Removal percentage of amoxicillin (AMX) from laboratory-grade water in the presence of a $Mg_2Al–NO_3$-LDH over time. Initial [AMX] = 100 μg/L, initial [LDH] = 0.2 g/L; T = 20 °C; continuous stirring; dark. Line of best fit included as a guide for the eyes only.

3.1.2. *Comparison to other sorbent materials*

Similarly, favourable sorption resulting in the removal of AMX from laboratory-grade water using a different MgAl-LDH has been reported (Table 1). (Elhaci et al., 2020) The authors reported a greater equilibrium sorption capacity, q_e, of AMX on to the LDH, with a q_e of 30.42 mg/g reported, than the sorption capacities found in this work, 0.54 ± 0.018 mg/g for standard reaction conditions. Additional studies with LDH-based composite materials reach a q_e of 49.66 mg/L for a concrete based-LDH material (Liu et al., 2022) and 138.3 mg/g for a cellulose-LDH composite (Yang et al., 2020). The greater sorption capacities for these literature examples compared to this study are due to the elevated AMX starting concentrations (≥mg/L) used in the literature, compared to 100 μg/L AMX concentration used in this work. This results in an increased concentration of AMX to LDH sorbent mass ratio at the start of the experiments, with the difference in relationship between concentration of pollutant and mass of sorbent material controlling the maximum possible experimental removal capacity which can be observed. Whilst a decreased sorption capacity of AMX is reported for $Mg_2Al–NO_3$-LDH than other literature studies, the sorption capacity would be improved if a greater starting AMX concentration to LDH mass ratio was used. Therefore, conclusions cannot be made about a reduced performance of $Mg_2Al–NO_3$-LDH reported here in a real-world application compared to other studied sorbent materials. It also demonstrates that it is important to consider the removal of antibiotics at environmentally-relevant concentrations, which better represent the conditions sorbent materials will be required to perform at in any widespread application, so as not to overestimate a material's sorption capacity (Ateia et al., 2020). Such an overestimation of sorption performance can also result in misleading results regarding the use of LDH or indeed any sorbent material for wastewater treatment in practice.

3.1.3. *Role of sorbent mass*

The role of changing the mass of LDH used in the removal experiments and resulting AMX removal and sorption capacity was investigated (Fig. 2a–b). Understanding the relationship between the adsorbent mass and pollutant sorption is important to the reactor design and developing a cost-effective system for any large-scale application of LDH as a sorbent material for pollutant removal from water. The removal percentage of AMX increased slightly from 94.53 ± 4.30 %–99.90 % as the mass of LDH was increased from 0.2 to 0.64 g/L. A decrease in the sorption capacity (mg/g) was observed with increasing LDH mass, from 0.16 mg/g to 0.54 ± 0.018 mg/g. The change in sorption capacity is due to the increasing number of sorption sites available on the LDH as increasing mass of sorbent material is used. Given the same starting concentration of AMX, a lower proportion of sorption sites will be occupied, resulting in a lower sorption capacity (xing Zha et al., 2013). The difference between the removal percentages of AMX between the LDH dosages of 0.2 and 0.64 g/L was ~5 %, hence it was decided that 0.2 g/L of LDH was sufficient for AMX removal and carried forward for all further investigations. Scaling-up the system to an industrial process would require further optimization of the mass of LDH used, for both economic and sustainability considerations.

3.1.4. *Role of AMX concentration*

The impact of changing the starting concentration of AMX was also investigated as changes in pollutant concentration can affect sorption performance as sorption is a mass transfer driven process (Wang et al., 2020). Four different concentrations, between 500 and 10 μg/L were investigated (Fig. 2c–d). In each case the removal of AMX was found to be between 94.53 ± 4.30 and 98.23 ± 0.47 %, indicating that the starting concentration did not impact the removal performance of the $Mg_2Al–NO_3$-LDH in laboratory-grade water. As found for the impact of changing the mass of LDH used in the sorption experiments, a variation in the sorption capacity of the $Mg_2Al–NO_3$-LDH was observed with the

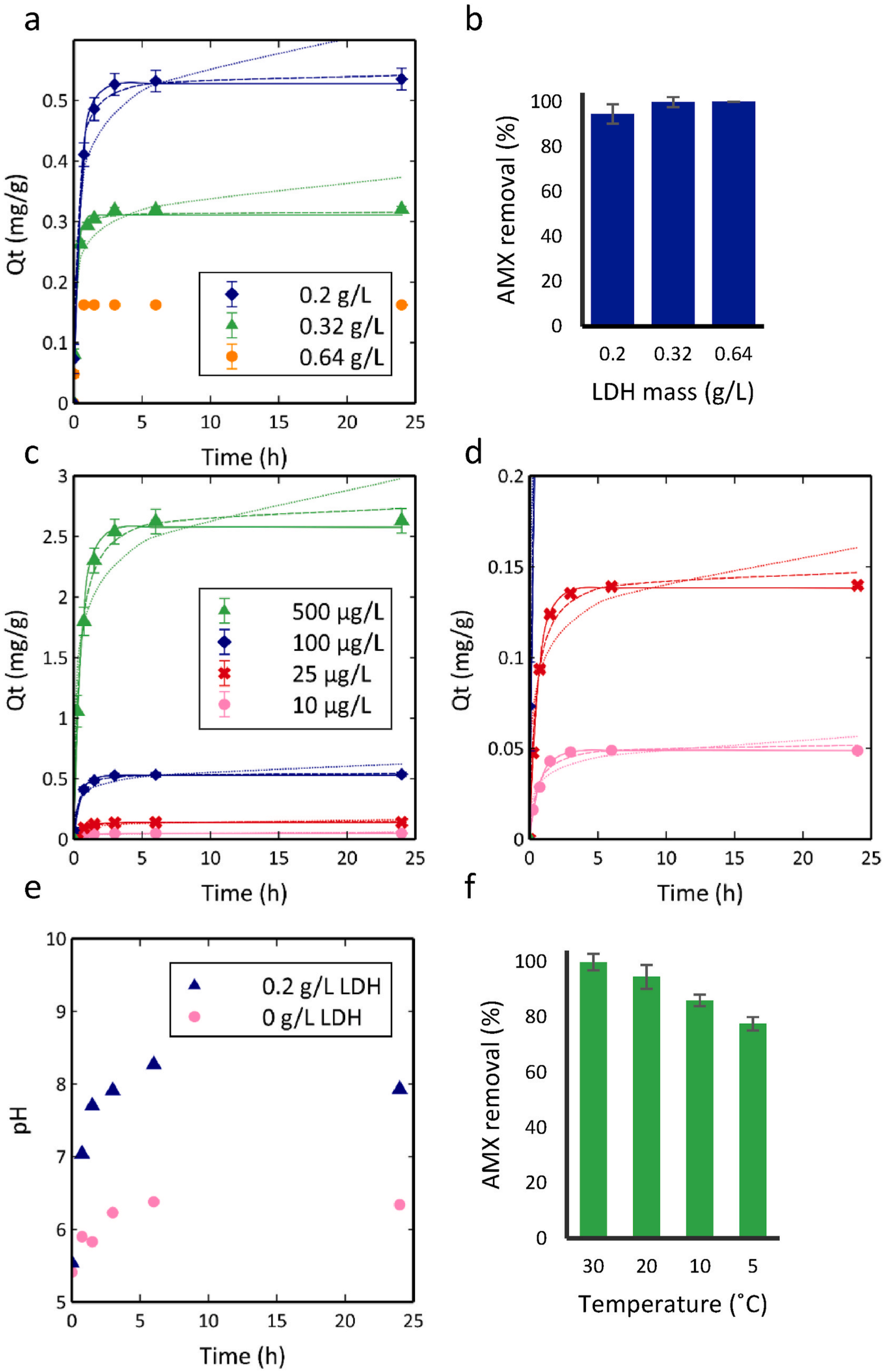


Fig. 2. a) Sorption capacity, q_t (mg/g), of amoxicillin (AMX) over 24 h with varying mass of LDH in laboratory-grade water; b) corresponding removal percentage of AMX (%) after 24 h with varying mass of LDH in laboratory-grade water; c & d) Sorption capacity, q_t, (mg/g) of AMX over 24 h with varying starting concentration of AMX in laboratory-grade water; e) change in solution pH in standard experimental set up with 0.2 g/L and 0 g/L LDH in laboratory-grade water; f) Removal percentage (%) of AMX from laboratory-grade water after 24 h with varying solution temperature. Sorption capacity graphs (a, c & d) display kinetics models: – pseudo-second order (PSO); - - pseudo-first order (PFO); ···· Elovich. Standard reaction conditions in laboratory-grade water, constant unless otherwise indicated: initial [AMX] = 100 µg/L, initial [LDH] = 0.2 g/L; T = 20 °C; continuous stirring; dark.

Table 1

Sorption capacities, q_e (mg/g), for various sorbent materials including LDH-based sorbent materials for the removal of amoxicillin (AMX).

Sorbent material	Experimental sorption capacity, q_e (mg/g)	Ref
MgAl–NO_3-LDH	0.54	This work
MgAl-LDH	49.48	Elhaci et al. (2020)
MgFe-LDH	9.11	Phelipe de Lima et al. (2020)
Concrete based-LDH composite material	49.66	Liu et al. (2022)
Cellulose-LDH composite material	5.29	Yang et al. (2020)
Bentonite	45.04	xing Zha et al. (2013)
Polyethylene terephthalate microplastics	198.11	Lionetto et al. (2023)
Aged polyethylene	2.72	Fan et al. (2021)

change in starting concentration of AMX. An increase in the starting concentration of AMX resulted in an increase in the sorption capacity from 0.049 ± 0.001 mg/g to 2.63 ± 0.10 mg/g. This can be explained due to the greater mass of AMX (mg) removed by the same mass of LDH (0.05 g) across each of the experiments. As a removal percentage >95% was observed for each experiment, a clear trend between the sorption capacity of the LDH and the starting concentration of AMX can be observed. Further, these findings highlight that LDH is a suitable sorbent for remediation of AMX within the pollutant concentration ranges observed in the environment, which has been reported to be down to 6.94 μg/L in WWTP in Australia (Watkinson et al., 2009) and ~25 mg/L in untreated effluent from a pharmaceutical wastewater in China (Hu et al., 2022).

3.1.5. *Role of temperature*

Temperature is an important parameter on sorption behaviour due to the influence on mobility and solubility of the pollutant. This has implications to design and process conditions e.g. hydraulic retention time when adapting sorbent technology for WWTPs based globally e.g. UK compared to India. To understand the influence of temperature on AMX sorption by $Mg_2Al–NO_3$-LDH, removal experiments were carried out at temperatures between 5 and 30 °C, representing the majority of temperatures modelled for wastewater globally (Hart and Halden, 2020).

The removal of AMX decreased with decreasing solution temperature, from 99.82 ± 3.01 % to 77.56 ± 2.41 % for 30 °C to 5 °C respectively (Fig. 2f), indicating sorption of AMX onto the LDH is favoured at higher temperatures, i.e. removal higher at 30 °C compared to 5–20 °C for this system. This is explained due to increase in pollutant molecule mobility at increasing temperatures, resulting in a more favourable interactions between the AMX and the LDH, and is observed for the sorption of various different organic pollutants by LDHs (Yang et al., 2016). Temperature-dependent sorption data can be used to understand the thermodynamics of the sorption process, details in supplementary information.

Negative ΔG° values are observed at each temperature, indicating a thermodynamically favourable process due to the spontaneous nature of the adsorption process between $Mg_2Al–NO_3$-LDH and AMX pollutant (Table 2). (Doke and Khan, 2013) The decreasing value of ΔG° with increasing temperature indicates increasing spontaneity at higher temperatures, observed previously in the case of the sorption of AMX onto a MgAl-LDH (Elhaci et al., 2020). The calculated ΔG° between −19.05 and −5.77 kJ/mol for solution temperatures 5 to 30 °C respectively, indicate physisorption, where physisorption is typically characterised by a free energy of between −20 and 0 kJ/mol (Renault et al., 2008). Positive ΔS° (0.6 kJ mol^{-1} K^{-1}) indicates increased disorder at the LDH surface following sorption of the AMX. Positive ΔH° (164 kJ/mol) shows the process to be endothermic, in agreement with the findings of increased pollutant removal at elevated temperatures.

Table 2

Thermodynamic parameters for the removal of AMX onto $Mg_2Al–NO_3$-LDH in laboratory-grade water at various temperatures. Standard reaction conditions in laboratory-grade water initial [AMX] = 100 μg/L, initial [LDH] = 0.2 g/L; continuous stirring; dark. ΔG°- Gibbs free energy change; ΔH° - standard enthalpy; and ΔS° - standard entropy.

Temperature (K)	ΔG° (kJ/mol)	ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K^{-1})
302.05	−19.05	164.0	0.60
293.45	−13.01		
285.15	−8.18		
281.15	−5.77		

3.1.6. *Sorption kinetics*

Sorption kinetics are important to understand the rate of uptake of the pollutant by the sorbent material (Yang et al., 2016). The AMX sorption data has been modelled by three non-linear kinetic models, the pseudo-first order (PFO), pseudo-second order (PSO) and Elovich model (details in supplementary information). The sorption of AMX by the $Mg_2Al–NO_3$-LDH is well described by both the PFO and PSO models across all experimental conditions considered in this study (Table 3), when comparing the R^2 values for each model. The removal of AMX by the LDH is poorly described by the Elovich model ($R^2 < 0.90$ for most experimental conditions), indicating that the LDH can be characterised as having a homogenous surface with limited interactions between the AMX molecules upon sorption to the LDH (Wu et al., 2009). The PFO model typically considers experimental conditions in which the sorbate uptake is directly proportional to the solute concentration and the amount of LDH is the system, with the PSO indicating some chemisorption influence (Yang et al., 2016). As the thermodynamics in Table 2 indicate the sorption process of AMX on to $Mg_2Al–NO_3$-LDH is dominated by a physisorption mechanism, the data is likely more accurately represented by the PFO rate constant, k_1. The PFO model has been found to best describe the sorption of pharmaceuticals by LDH, including oxytetracycline removal by ZnFe-LDH (Zaher et al., 2020).

Comparing the PFO rate constants, k_1, under different experimental conditions the rate is found firstly to increase with increasing mass of LDH used in the sorption experiment, reaching 0.073 min^{-1} for 0.32 g/L of LDH, and secondly with increasing solution temperature, 0.053 min^{-1} for AMX removal at 30 °C. This is explained through the improved mass transfer under these conditions, which increases the probability of the interaction between the sorbent and the sorbate in the system (Wang et al., 2020). At decreasing temperatures, the rate constant (k_1) decreases to 0.013 min^{-1}, indicating rate of removal is reduced at lower temperatures, resulting from reduced mass transfer of the AMX in the system.

There is a less pronounced trend for the removal of different starting concentrations of AMX. Decreasing the starting concentrations of AMX from 100 to 10 μg/L shows a decrease in k_1 from 0.033 to 0.022 min^{-1}, which would be described again through decreasing mass transport as a result of lower pollutant concentrations in the liquid phase. However, when the concentration of AMX is increased to 500 μg/L the k_1 rate constant appears between these two values (0.029 min^{-1}). On closer consideration the removal data appears to be better modelled by the PSO rate model when the starting concentration of AMX is 500 μg/L, with the R^2 for the PSO 0.986 is compared to an R^2 of 0.979 for the PFO. This may indicate that different sorption mechanisms are occurring at higher concentrations of AMX present in the solution, which explains the deviation in pattern to the PFO rate constants at increasing pollutant concentrations. This is important to consider and explore further depending on the concentration of pollutant in the final wastewater effluent to be treated by the LDH sorbent material.

Table 3

Maximum experimental sorption capacity ($q_{e,\ exp}$). Pseudo-first order (PFO), pseudo-second order (PSO) and Elovich models, for a range of different experimental conditions, for the sorption of AMX from laboratory-grade water by $Mg_2Al–NO_3$-LDH. Calculated through non-linear fittings. q_e is the equilibrium uptake of AMX (mg g-1), k_1 (min^{-1}) is the PFO rate constant, k_2 (g mg^{-1} min^{-1}) is the PSO rate constant, andα (mg g^{-1} min^{-1}) and β (g mg^{-1}) are constants related to the Elovich model.

Experimental conditions				*Pseudo-second order PSO*			*Pseudo-first order PFO*			*Elovich*		
Temp (°C)	LDH (g/L)	AMX (μg/L)	$q_{e,exp}$ (mg/g)	R (Litskas et al., 2018)	$q_{e,cal}$ (mg/g)	k_2 (g mg^{-1} min^{-1})	R (Litskas et al., 2018)	$q_{e,cal}$ (mg/g)	k_1 (min^{-1})	R (Litskas et al., 2018)	β (mg/g)	A (mg g^{-1} min^{-1})
20	0.20	100	0.52	0.990	0.546	0.154	0.979	0.528	0.033	0.902	14.531	0.403
	0.32	100	0.32	0.984	0.316	0.868	0.993	0.311	0.073	0.987	28.852	1.144
	0.64	100	0.16	*Kinetics not modelled due to removal reaching equilibrium before first data point*								
	0.20	500	2.63	0.986	2.775	0.016	0.979	2.577	0.029	0.786	2.895	1.336
	0.20	25	0.14	0.972	0.150	0.255	0.997	0.138	0.026	0.766	50.158	0.044
	0.20	10	0.049	0.958	0.053	0.618	0.988	0.049	0.022	0.769	134.851	0.011
30	0.20	100	0.54	0.953	0.566	0.158	0.992	0.536	0.053	0.726	21.489	12.054
10	0.20	100	0.39	0.983	0.423	0.039	0.997	0.381	0.013	0.892	13.655	0.021
5	0.20	100	0.40	0.999	0.424	0.062	0.998	0.389	0.018	0.986	15.635	0.052

3.2. *Removal behaviour of AMX from wastewater effluent*

3.2.1. *Change in AMX concentration in wastewater effluent in presence of LDH*

Whilst excellent removal of AMX by $Mg_2Al–NO_3$-LDH is observed from laboratory-grade water (95–99 % depending on study conditions), moving up the technology readiness levels requires evaluating the removal of AMX from environmental waters to understand application potential. Therefore, to understand LDH sorbent performance in alternative liquid phases, for the first-time sorption experiments were carried out with AMX-doped WWE as the liquid phase in place of laboratory-grade water.

Wastewater effluent is complex, containing multiple constituents or "multi-pollutants". There is natural variation in WWE composition (see water quality parameters in Table S2) within a single sampling site, due to seasonal variation, weather events, and the changing incoming wastewaters received by the WWTP. Therefore, to address the natural variation in WWE, AMX removal experiments were carried out in WWE sampled on three different days (between October 2022 and May 2023).

A similar behavioural trend of AMX was observed in all three WWE samples, both in control and removal experiments (Fig. S2) where the controls contained no LDH sorbent material. A decrease in concentration of AMX in the WWE in the presence of $Mg_2Al–NO_3$-LDH is observed, with an average AMX concentration of 78.10 ± 2.08 μg/L after 24 h (Fig. 3a). A decrease in average AMX concentration was observed in the WWE samples used as a control (no LDH present), with an AMX concentration of 66.01 ± 1.82 μg/L after 24 h. The difference in final concentrations of AMX in the removal and control experiments ($p < 0.05$) indicates that the presence of the LDH is impacting the behaviour of AMX in the WWE.

The percentage decreases across each of the WWE control experiments ranges from 23.86 ± 6.07% to 26.33 ± 8.93% when no is LDH present, compared to a range of 3.51 ± 4.25% to 13.39 ± 5.53% for the removal experiments in the presence of $Mg_2Al–NO_3$-LDH over 24 h, compared to the starting concentration of AMX recorded at $t = 0$ h.

The same pattern of a greater removal of AMX from the water matrix is observed in the control samples compared to the removal experiments in the present of LDH (0.2 g/L) across all three WWE samples. This demonstrates that a decrease in AMX concentration from the WWE is not solely a result of sorption of the AMX onto the LDH. Further, as AMX removal from WWE is greater with no LDH present it illustrates that the presence of LDH is impacting the degree of removal of AMX in solution, as shown for the final concentrations of AMX (μg/L) in the WWE. It has been reported in the literature that characteristics of water, including temperature and pH, can impact hydrolysis and subsequent removal of AMX by abiotic degradation in water matrices (Hirte et al., 2016; Fawaz et al., 2021). As both pH and temperature of the WWE are similar in the removal and control experiments, with and without LDH being present (Fig. 3c), it is unlikely that these factors are influencing the difference in AMX removal behaviour.

The removal experiment was also repeated with a greater starting mass of LDH of 1 g/L (compared to 0.2 g/L) and a similar behaviour of decreasing AMX concentration from initial concentration was still observed, resulting in a final concentration of AMX of 77.99 ± 2.22 μg/L (Fig. 3b). However, increasing the mass of LDH shows no improvement to the removal of AMX from the WWE. This contrasts with observations for sorption of AMX from laboratory-grade water, where increasing the mass of LDH influenced the sorption of AMX (Fig. 2b), including an apparent increase in the rate of sorption of AMX (Table 3).

The pH of the WWE in the presence of 0.2 g/L LDH (Fig. 3c) was

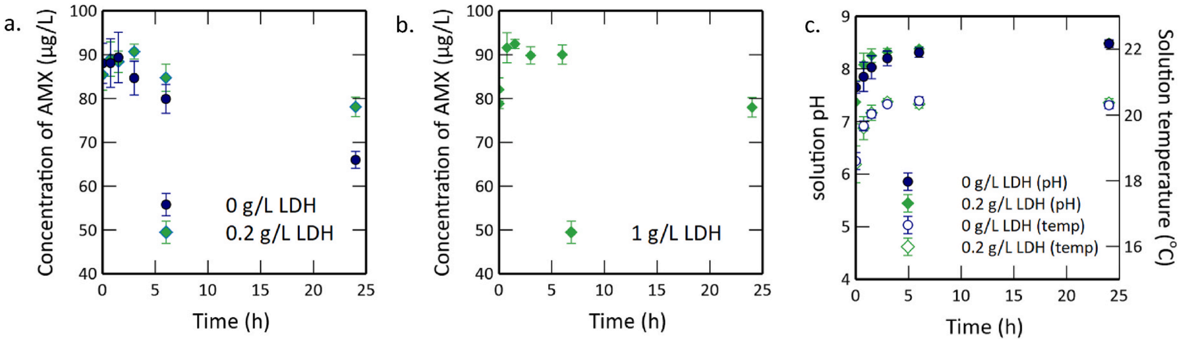


Fig. 3. a) Change in concentration of amoxicillin (AMX) (μg/L) over 24 h in wastewater effluent (WWE), with 0.2 g/L MgAl-LDH (removal) and 0 g/L LDH (control) in WWE. Error bars calculated from 3 different WWE samples collected on different days from Stoke Bardolph water treatment plant; b) Change in concentration of AMX (μg/L) over 24 h in WWE, with 1.0 g/L LDH (0.2 g/L) (removal), from one WWE sample c) Change in WWE pH (filled data points) filled and temperature (outlined data points) over 24 h with 0.2 g/L and 0 g/L LDH during sorption experiments. Reaction conditions: initial [AMX] = 100 μg/L, T = 20 °C; continuous stirring, dark. Error bars calculated from 3 different WWE samples collected on different days apart from in the case of 1 g/L LDH removal data.

found to stabilise at pH 8.49 ± 0.04, comparable to the pH under the same experimental conditions in laboratory-grade water (Fig. 2e). For 1 g/L of LDH the final pH was found to be comparable at 8.57. Therefore, it would be expected that the speciation of the AMX and LDH surface charge would result in favourable sorption interactions between with anionic LDH and positive charged LDH surface, irrespective of the LDH mass used. However, as the removal of AMX is not observed in WWE, as found in laboratory-grade water (~95%) in the presence of the $Mg_2Al–NO_3$-LDH, it infers that a proportion of the sorption sites on the LDH are unavailable for AMX uptake, due to being blocked by the sorption of other constituents present in the WWE. Common WWE constituents such as humic and fulvic acids have been shown to be rapidly removed from aqueous matrices by a MgAl-LDH (Vreysen and Maes, 2008). Additional pollutants occurring in WWE, including metals and anionic salts, have also been reported to reduce the removal capacity of LDH materials for the removal of organic pollutants (Chen et al., 2019; Jing et al., 2019). Therefore, it can be rationalised that similar processes taking place in this work result in the lack of AMX sorption by LDH in WWE due to competition for sorption sites.

There are studies reporting AMX removal from complex industrial wastewaters by sorbent materials in the literature. However, knowledge regarding the degradation of AMX in control experiments in environmental waters raises some uncertainties. For example, modified bentonite organoclay was reported to remove AMX (82–88 %) from industrial wastewater (xing Zha et al., 2013). However, control experiments, considering the concentration change of AMX without the presence of any sorbent material are not discussed in the study. Based on the control experiments using WWE for this study and knowledge that amoxicillin can undergo degradation in environmental waters via various mechanisms including due to the presence of β-lactamases, it is unclear if the reported AMX removal can be solely contributed to sorption or if a proportion is due to transformation of AMX in the industrial wastewater (Ecke et al., 2023). A similar scenario is reported for the removal of AMX from 5 different wastewaters by a Zn-carbon nanotube composite sorbent material, who reported 100 % of AMX is removed in each wastewater (Chaba and Nomngongo, 2019). However, in this study relevant control experiments considering the change in AMX concentration in water samples without the sorbent material are not discussed, hence the decrease in AMX concentration may partially be due to biotic or abiotic degradation.

Beyond sorption by LDH during removal experiments, and in the case of the control experiments (without LDH present), there are several possible transformation pathways for AMX in environmental waters, including abiotic (e.g. hydrolysis) and biotic processes (e.g. enzymatic biotransformation) (Hirsch et al., 1999). In addition, some organic pollutants have shown sorption to the suspended solids present in environmental waters (Aminot et al., 2018). The low concentration of suspended solids in filtered-WWE used in this work (≤3 mg/L) suggests that this outcome is unlikely. Complexation of antibiotics to metals in WWE has also been observed, which would also contribute to a decrease the concentration of AMX present in the WWE (Khurana et al., 2021). Therefore, it is likely that a complex combination of abiotic and biotic transformation processes are contributing to the decrease in AMX concentration in the WWE in both control (without LDH) and removal (with LDH) experiments.

3.2.2. *LDH sorption of metals in WWE*

The coexistence of pollutants in environmental waters, including both metals and pharmaceuticals, can have consequences on a materials sorption performance. Interactions between multiple pollutants are either synergistic, antagonistic, or independent in nature, or may be a combination of interactions, distinct for each pollutant (Zhai et al., 2023). Therefore, it was hypothesised that metals present in the WWE may be competing with AMX for the sorption sites on the surface of the LDH, as it is widely reported that heavy metals can also be removed from water by LDH sorbents (Guan et al., 2022). To evaluate this phenomenon, analysis of the change in concentration of selected metals present in the WWE following exposure to LDH for 24 h was carried out (Fig. 4), with the details summarised in Table 4.

A remarked decrease in the concentration of divalent metals, including Cu^{2+}, Zn^{2+}, Mn^{2+}, and Fe^{2+}, after exposure of the WWE to $Mg_2Al–NO_3$-LDH for 24 h, both with 100 μg/L AMX (WWE-B) and without AMX (WWE-C) present. Most notable is the decrease in Zn^{2+} from 109.16 ± 1.13 μg/L to 16.73 ± 0.35 μg/L and Mn^{2+} from 57.05 ± 0.97 μg/L to 11.99 ± 0.34 μg/L over 24 h with the presence of LDH, corresponding to removal percentages of 84.67 % and 78.99 % respectively.

The addition of 100 μg/L of AMX to the WWE does not appear to impact the trends in concentration change of metals in WWE (Fig. 4). For example, in the case of Mn^{2+}, the concentrations without LDH present are found to be 57.68 ± 1.70 μg/L without AMX (WWE-E) and 56.84 ± 2.68 μg/L with AMX (WWE-D). Whilst with LDH, Mn^{2+} are found to be decreased to 12.18 ± 0.23 μg/L without AMX (WWE-C) and 11.99 ± 0.34 μg/L with AMX (WWE-B), indicating the presence of AMX in the WWE is not impacting the change in metal concentrations in WWE. As a decrease in metal concentrations in WWE over 24 h is not observed in the samples without LDH present (both in WWE-D and WWE-E), the decreases in metal concentrations in WWE is not a naturally occurring process and is directly attributable to the presence of LDH.

Research has shown that LDHs can remove divalent metals from water matrices through mechanisms including surface complexation, (co)precipitation, and isomorphic substitutions (Liang et al., 2013). For example, the removal of both Cu and Zn from a cattle footbath using a CaAl-EDTA-LDH (Williams et al., 2019). Further, MgAl-LDH intercalated with sulfonated lignin has shown removal of Cu from deionised water (Huang et al., 2015). There are also examples in the literature of Zn removal by $MgAl–NO_3$-LDH (Komarneni et al., 1998), MgFe-LDH from a $NaNO_3$ solution (Hudcová et al., 2018) and by CaAl–Cl-LDH from various waters including metal-rich wastewater (Zhang et al.,

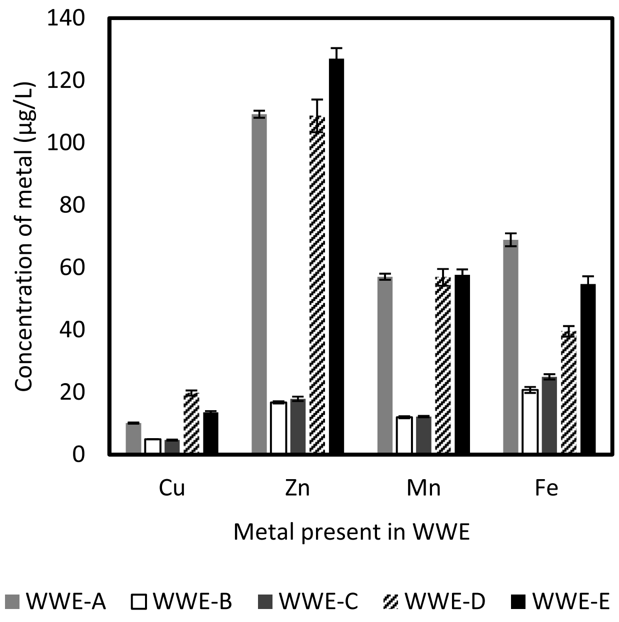


Fig. 4. Concentration of selected metals in municipal wastewater effluent (WWE) for samples: WWE-A, WWE at t = 0 h; WWE-B, WWE + LDH + AMX at t = 24 h; WWE-C, WWE + LDH at t = 24 h; WWE-D, WWE + AMX at t = 24 h; WWE-E WWE at t = 24 h (left to right on the graph for each metal). WWE sampled from Stoke Bardolph water treatment plant during May 2023. More details of sample composition shown in Table 4. Reaction conditions: initial [AMX] = 100 μg/L, LDH 0.2 g/L, T = 20 °C; continuous stirring, dark.

Table 4
Characteristics of the wastewater effluent (WWE-3, Table S2) prior and following 24 h exposure to AMX (100 μg/L and 0.2 g/L $Mg_2Al–NO_3$-LDH. All experimental samples were kept under same conditions: T = 20 °C; continuous stirring; dark. Wastewater effluent sampled from Stoke Bardolph treatment plant in May 2023.

Sample ID	WWE-A	WWE-B	WWE-C	WWE-D	WWE-E
Components in experimental solution	WWE only	WWE + LDH + AMX	WWE + LDH	WWE + AMX	WWE only
Time (h)	0	24	24	24	24
LDH (g/L)	NA	0.2	0.2	0	0
AMX (μg/L)	NA	100	0	100	0
pH	7.61	8.54	8.56	8.53	8.52

2012). Similarly, Mn removal from deionised water by MgAl-LDH intercalated with DTPA has been reported (Huang et al., 2019).

The impact of the removal of metals from the WWE onto the LDH materials is multi-fold. Firstly, removal of metals from the WWE is likely contributing to the difference in the sorption performance of the $Mg_2Al–NO_3$-LDH for AMX removal in different water matrices, and ultimately the lack of sorption of AMX from WWE to the LDH. It is likely the decrease in metal concentration in WWE is due to the sorption of the metals on the surface of the LDH. This blocks the sorption sites which would otherwise be available for the sorption of antibiotics such as AMX, with such an impact being previously reported for the removal of the antibiotic oxytetracycline by a CuMnAl-hydroxide (Eniola et al., 2020). Additionally, metal-ion catalysis of the hydrolysis of similar β-lactam antibiotics has been reported, with it suggested that divalent transition metals such as Zn^{2+}, Mn^{2+}, Cu^{2+}, Ni^{2+} and Co^{2+} are able to catalyse the transformation pathway (Gensmantel et al., 1980; Huang et al., 2017). Similarly, the hydrolysis kinetics and pathways of AMX degradation in various environmental waters has been shown to be impacted by the presence of heavy metals (including Cu and Zn) within the water matrix (Ecke et al., 2023). Therefore, it can be postulated that the decrease of divalent metal concentrations in the WWE in presence of $Mg_2Al–NO_3$-LDH is contributing to the reduction in the rate of hydrolysis of AMX in the WWE. The greater AMX concentration present in the WWE after 24 h in removal experiments with LDH present, compared to control experiments (no LDH present) can be explained through this phenomenon. The WWE samples without any LDH has a higher concentration of divalent metals, which results in the hydrolysis of AMX being catalysed to a greater degree.

Further to deepening the understanding the application of MgAl-LDH as a sorbent material for the removal of AMX from water, this study highlights the complexity of multipollutant behaviour in environmental waters on sorption processes. The addition of a sorbent material in water treatment will likely impact the concentration of so-called untargeted pollutants, which will have implications to downstream wastewater treatment, due to changes to the expected water matrix composition. For example, the metal removal from WWE may have unintended consequences on the antibiotics present in the environment, which are not easily predicted. Changing metal concentrations may alter the transformation pathways of the antibiotics, resulting in alternative transformation products at elevated concentrations compared to if the metals are not removed from the WWE. Different transformation products may have different toxicity to biodiversity (Maculewicz et al., 2022). In addition, antibiotics are known to undergo metal complexation in WWE, forming antibiotic-metal complexes, which can display increased antimicrobial activity due to altered physiochemical properties (Khurana et al., 2021). By changing the concentrations of metals in WWE (in this case, through addition of a sorbent material), it is possible that the nature of metal complexation taking place will be altered, again with unknown consequences. To understand this phenomenon in more detail, further work should be considered the understand the impact of various independent components in the WWE on the sorption of AMX. In addition, alternative environmental waters (e.g. hospital wastewater), with differing concentrations of AMX should be used, to understand how sorption of AMX changes in the presence of different components in the WWE.

4. Conclusion

This study analysed the removal of AMX (10–500 μg/L) from laboratory-grade water, reaching removal percentages >95%, using a continuously synthesised $Mg_2Al–NO_3$-LDH. Comparable removal of AMX was not observed when WWE was used as the liquid phase under the same experimental conditions in a batch sorption set up. This lack of sorption in WWE is likely due to the saturation of sorption sites by naturally occurring constituents present in the WWE.

The preferential removal of divalent metals from the WWE over an antibiotic by an LDH is reported for the first time. A greater decrease in AMX concentration is observed in the WWE without the presence of LDH, compared to the 'removal' experiments (resulting in concentrations 66.01 ± 1.82 μg/L of compared to 78.10 ± 2.08 μg/L, at 24 h, respectively). It is proposed that this is due to the difference in the metal concentrations in the WWE with and without LDH present, as metals are known to catalyse the hydrolysis of AMX and result in the formation of antibiotic-metals complexes. Whilst LDH materials require further development to realise the sorption of AMX from complex environmental waters, there is the possibility of exploiting the removal of metals from WWE by LDH in the treatment of metal polluted waters (with or without organic pollutants present). Further, it is possible that there may be different LDH sorption behaviour in a continuous system set-up, requiring further investigation.

A major issue with lab-scale sorption studies is the lack of consideration of removal from environmental water matrices under realistic application conditions, possibly indicating a performance of sorbent materials which may not be realised in water treatment applications. It is recommended that in the future lab-scale sorption experiments evaluating the performance of any new sorbent materials (not just LDH sorbent materials) should consider the following to ensure the results are as relevant as possible to future water treatment applications:

- *Removal of pollutants, particularly emerging contaminants such as antibiotics, at realistic environmental concentrations (<mg/L)* as experiments with pollutant concentrations higher than observed in the environment may lead to potentially misleading conclusions about sorbent material performance.
- *Impact on the removal of pollutants when sorption experiments are carried out in complex environmental waters, when compared to laboratory-grade water.* This will allow for a deeper understanding of how the complexity of constituents present in environmental waters influence sorption behaviour of the target pollutant/s, as discussed in this work.
- *How sorbent materials are interacting with the water beyond simply evaluating the change in concentration of the target pollutant/s of interest.* Sorbent materials may cause secondary pollution of the water due to partial dissolution of the sorbent material, with potential knock-on detrimental impacts on the environment and influence where in a WWTP the sorption technology is located. Secondly, any removal of other constituents naturally present in the water beyond the target pollutant due to the presence of the sorbent materials could be detrimental to the removal of the target pollutant, as shown in this work. Further both outcomes (secondary pollution or removal of other constituents in wastewater) would change the composition of the water, which can have unintended impacts on the complex environmental processes taking place in the water, such as abiotic and biotic pollutant degradation.

Funding

This work was funded and supported by the Engineering and Physical Sciences Research Council (EPSRC) Centre for Doctoral Training in Sustainable Chemistry: Atoms-2-Products an Integrated Approach to Sustainable Chemistry [grant number: EP/L015633/1], the EPSRC BIOTRANSFOROMICS: Bioanalysis to engineer understanding in wastewater treatment [grant number: EP/M022234/1], and EPSRC Cognitive Chemical Manufacturing [grant number: EP/R032807/1].

CRediT authorship contribution statement

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

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.

Acknowledgements

All authors would like to thank Severn Trent Water Ltd. for permission and access to wastewater effluent from the Stoke Bardolph wastewater treatment process.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2024.143546.

Data availability

Data will be made available on request.

References

Álvarez-Ayuso, E., Nugteren, H.W., 2005. Purification of chromium(VI) finishing wastewaters using calcined and uncalcined Mg-Al-CO3-hydrotalcite. Water Res. 39, 2535–2542.

Aminot, Y., Fuster, L., Pardon, P., Le Menach, K., Budzinski, H., 2018. Suspended solids moderate the degradation and sorption of waste water-derived pharmaceuticals in estuarine waters. Sci. Total Environ. 612, 39–48.

Ateia, M., Helbling, D.E., Dichtel, W.R., 2020. Best practices for evaluating new materials as adsorbents for water treatment. ACS Mater. Lett. 2, 1532–1544.

aus der Beek, T., Weber, F., Bergmann, A., Hickmann, S., Ebert, I., Hein, A., Küster, A., 2016. Pharmaceuticals in the environment—global occurrences and perspectives. Environ. Toxicol. Chem. 35, 823–835.

Braterman, P.S., Xu, Z.P., Yarbery, F., 2005. In: Auerbach, S.M., Carrado, K.A., Dutta, P. K. (Eds.), Handbook of Layered Materials. CRC Press, New York, pp. 363–457.

Burtch, N.C., Jasuja, H., Walton, K.S., 2014. Water stability and adsorption in metal–organic frameworks. Chem. Rev. 114, 10575–10612.

Cardinale, A.M., Carbone, C., Consani, S., Fortunato, M., Parodi, N., 2020. Layered double hydroxides for remediation of industrial wastewater from a galvanic plant. Crystals 10, 443.

Chaba, J.M., Nomngongo, P.N., 2019. Effective adsorptive removal of amoxicillin from aqueous solutions and wastewater samples using zinc oxide coated carbon nanofiber composite. Emerging Contam. 5, 143–149.

Chen, C., Ruengkajorn, K., Buffet, J.-C., O'Hare, D., 2018. Water adsorbancy of high surface area layered double hydroxides (AMO-LDHs). RSC Adv. 8, 34650–34655.

Chen, Y., Jing, C., Zhang, X., Jiang, D., Liu, X., Dong, B., Feng, L., Li, S., Zhang, Y., 2019. Acid-salt treated CoAl layered double hydroxide nanosheets with enhanced adsorption capacity of methyl orange dye. J. Colloid Interface Sci. 548, 100–109.

Chow, L.K.M., Ghaly, T.M., Gillings, M.R., 2021. A survey of sub-inhibitory concentrations of antibiotics in the environment. J. Environ. Sci. 99, 21–27.

Clark, I., Smith, J., Gomes, R., Lester, E., 2019. Continuous synthesis of Zn2Al-CO3 layered double hydroxides for the adsorption of reactive dyes from water. J. Environ. Chem. Eng. 7, 103175.

Council of the EU, Press Release. Council adopts position on new rules for more efficient treatment of urban wastewater. https://www.consilium.europa.eu/en/press/press-releases/2023/10/16/council-adopts-position-on-new-rules-for-a-more-efficient-treatment-of-urban-wastewater/. (Accessed 23 October 2023).

da Silva, A.F., Duarte, J.L. da S., Meili, L., 2021. Different routes for MgFe/LDH synthesis and application to remove pollutants of emerging concern. Sep. Purif. Technol. 264, 118353.

Doke, K.M., Khan, E.M., 2013. Adsorption thermodynamics to clean up wastewater; critical review. Rev. Environ. Sci. Bio/Technol. 12, 25–44.

Dotto, G.L., McKay, G., 2020. Current scenario and challenges in adsorption for water treatment. J. Environ. Chem. Eng. 8, 103988.

Ecke, A., Westphalen, T., Retzmann, A., Schneider, R.J., 2023. Factors affecting the hydrolysis of the antibiotic amoxicillin in the aquatic environment. Chemosphere 311, 136921.

El Hassani, K., Beakou, B.H., Kalnina, D., Oukani, E., Anouar, A., 2017. Effect of morphological properties of layered double hydroxides on adsorption of azo dye Methyl Orange: a comparative study. Appl. Clay Sci. 140, 124–131.

Elhaci, A., Labed, F., Khenifi, A., Bouberka, Z., Kameche, M., Benabbou, K., 2020. MgAl-Layered double hydroxide for amoxicillin removal from aqueous media. Int. J. Environ. Anal. Chem. 15, 1–23.

Eniola, J.O., Kumar, R., Al-Rashdi, A.A., Barakat, M.A., 2020. Hydrothermal synthesis of structurally variable binary CuAl, MnAl and ternary CuMnAl hydroxides for oxytetracycline antibiotic adsorption. J. Environ. Chem. Eng. 8, 103535.

European Chemical Society, Elem. Scarcity – EuChemS period. Table. https://www.euchems.eu/euchems-periodic-table/. (Accessed 26 September 2023).

Fan, X., Gan, R., Liu, J., Xie, Y., Xu, D., Xiang, Y., Su, J., Teng, Z., Hou, J., 2021. Adsorption and desorption behaviors of antibiotics by tire wear particles and polyethylene microplastics with or without aging processes. Sci. Total Environ. 771, 145451.

Fawaz, S., Merzouk, M., Barton, S., Nabhani-Gebara, S., 2021. Stability of amoxicillin and clavulanic acid in separate containers for administration via a Y-site. Drug Des. Dev. Ther. 15, 3979–3984.

Gensmantel, N.P., Proctor, P., Page, M.I., 1980. Metal-ion catalysed hydrolysis of some β-lactam antibiotics. J. Chem. Soc., Perkin Trans. 2, 1725–1732.

Georgin, J., Franco, D.S.P., Meili, L., Dehmani, Y., dos Reis, G.S., Lima, E.C., 2023. Main advances and future prospects in the remediation of the antibiotic amoxicillin with a focus on adsorption technology: a critical review. J. Water Process Eng. 56, 104407.

Goh, K.-H., Lim, T.-T., 2010. Influences of co-existing species on the sorption of toxic oxyanions from aqueous solution by nanocrystalline Mg/Al layered double hydroxide. J. Hazard Mater. 180, 401–408.

Goh, K.-H., Lim, T.-T., Dong, Z., 2008. Application of layered double hydroxides for removal of oxyanions: a review. Water Res. 42, 1343–1368.

Guan, X., Yuan, X., Zhao, Y., Wang, H., Wang, H., Bai, J., Li, Y., 2022. Application of functionalized layered double hydroxides for heavy metal removal: a review. Sci. Total Environ. 838, 155693.

Hart, O.E., Halden, R.U., 2020. Modeling wastewater temperature and attenuation of sewage-borne biomarkers globally. Water Res. 172, 115473.

Hirsch, R., Ternes, T., Haberer, K., Kratz, K.-L., 1999. Occurrence of antibiotics in the aquatic environment. Sci. Total Environ. 225, 109–118.

Hirte, K., Seiwert, B., Schüürmann, G., Reemtsma, T., 2016. New hydrolysis products of the beta-lactam antibiotic amoxicillin, their pH-dependent formation and search in municipal wastewater. Water Res. 88, 880–888.

Homem, V., Alves, A., Santos, L., 2010. Amoxicillin degradation at ppb levels by Fenton's oxidation using design of experiments. Sci. Total Environ. 408, 6272–6280.

Hu, Y., Lei, D., Wu, D., Xia, J., Zhou, W., Cui, C., 2022. Residual β-lactam antibiotics and ecotoxicity to Vibrio fischeri, Daphnia magna of pharmaceutical wastewater in the treatment process. J. Hazard Mater. 425, 127840.

Huang, G., Wang, D., Ma, S., Chen, J., Jiang, L., Wang, P., 2015. A new, low-cost adsorbent: preparation, characterization, and adsorption behavior of Pb(II) and Cu (II). J. Colloid Interface Sci. 445, 294–302.

Huang, T., Fang, C., Qian, Y., Gu, H., Chen, J., 2017. Insight into Mn(II)-mediated transformation of β-lactam antibiotics: the overlooked hydrolysis. Chem. Eng. J. 321, 662–668.

Huang, M., Zhang, Y., Xiang, W., Zhou, T., Wu, X., Mao, J., 2019. Efficient adsorption of Mn(II) by layered double hydroxides intercalated with diethylenetriaminepentaacetic acid and the mechanistic study. J. Environ. Sci. 85, 56–65.

Hudcová, B., Veselská, V., Filip, J., Číhalová, S., Komárek, M., 2018. Highly effective Zn (II) and Pb(II) removal from aqueous solutions using Mg-Fe layered double hydroxides: comprehensive adsorption modeling coupled with solid state analyses. J. Clean. Prod. 171, 944–953.

Jing, C., Chen, Y., Zhang, X., Guo, X., Liu, X., Dong, B., Dong, F., Zhang, X., Liu, Y., Li, S., Zhang, Y., 2019. Low carbonate contaminative and ultrasmall NiAl LDH prepared by acid salt treatment with high adsorption capacity of methyl orange. Ind. Eng. Chem. Res. 58, 11985–11998.

Johnston, A.-L., Lester, E., Williams, O., Gomes, R.L., 2021. Understanding Layered Double Hydroxide properties as sorbent materials for removing organic pollutants from environmental waters. J. Environ. Chem. Eng. 9, 105197.

Johnston, A.-L., Lester, E., Williams, O., Gomes, R.L., 2024. Impacts of multi-pollutants on sulfonamide antibiotic removal from water matrices using layered double hydroxide sorbents. Environ. Technol. Innov. 33, 103490.

Kairigo, P., Ngumba, E., Sundberg, L.-R., Gachanja, A., Tuhkanen, T., 2020. Occurrence of antibiotics and risk of antibiotic resistance evolution in selected Kenyan wastewaters, surface waters and sediments. Sci. Total Environ. 720, 137580.

Kasprzyk-Hordern, B., Dinsdale, R.M., Guwy, A.J., 2008. The occurrence of pharmaceuticals, personal care products, endocrine disruptors and illicit drugs in surface water in South Wales, UK. Water Res. 42, 3498–3518.

Khurana, P., Pulicharla, R., Kaur Brar, S., 2021. Antibiotic-metal complexes in wastewaters: fate and treatment trajectory. Environ. Int. 157, 106863.

Komarneni, S., Kozai, N., Roy, R., 1998. Novel function for anionic clays: selective transition metal cation uptake by diadochy. J. Mater. Chem. 8, 1329–1331.

Larsson, D.G.J., de Pedro, C., Paxeus, N., 2007. Effluent from drug manufactures contains extremely high levels of pharmaceuticals. J. Hazard Mater. 148, 751–755.

Liang, X., Zang, Y., Xu, Y., Tan, X., Hou, W., Wang, L., Sun, Y., 2013. Sorption of metal cations on layered double hydroxides. Colloids Surfaces A Physicochem. Eng. Asp. 433, 122–131.

Lionetto, F., Esposito Corcione, C., Messa, F., Perrone, S., Salomone, A., Maffezzoli, A., 2023. The sorption of amoxicillin on engineered polyethylene terephthalate microplastics. J. Polym. Environ. 31, 1383–1397.

Litskas, V.D., Karamanlis, X.N., Prousali, S.P., Koveos, D.S., 2018. Effects of the antibiotic amoxicillin on key species of the terrestrial environment. Bull. Environ. Contam. Toxicol. 100, 509–515.

Liu, X., Yang, S., Feng, T., Zhong, H., Cao, S., Chen, Y., 2022. Removal of amoxicillin from water by concrete-based hydrotalcites: efficiency and mechanism. Process Saf. Environ. Protect. 163, 210–217.

Maculewicz, J., Kowalska, D., Świacka, K., Toński, M., Stepnowski, P., Białk-Bielińska, A., Dołżonek, J., 2022. Transformation products of pharmaceuticals in the environment: their fate, (eco)toxicity and bioaccumulation potential. Sci. Total Environ. 802, 149916.

Munonde, T.S., September, N.P., Mpupa, A., Nomngongo, P.N., 2022. Two agitation routes for the adsorption of Reactive Red 120 dye on NiFe LDH/AC nanosheets from wastewater and river water. Appl. Clay Sci. 219, 106438.

Murray, C.J.L., Ikuta, K.S., Sharara, F., Swetschinski, L., Robles Aguilar, G., Gray, A., Han, C., Bisignano, C., Rao, P., Wool, E., Johnson, S.C., Browne, A.J., Chipeta, M.G., Fell, F., Hackett, S., Haines-Woodhouse, G., Kashef Hamadani, B.H., Kumaran, E.A. P., McManigal, B., Agarwal, R., Akech, S., Albertson, S., Amuasi, J., Andrews, J., Aravkin, A., Ashley, E., Bailey, F., Baker, S., Basnyat, B., Bekker, A., Bender, R., Bethou, A., Bielicki, J., Boonkasidecha, S., Bukosia, J., Carvalheiro, C., Castañeda-Orjuela, C., Chansamouth, V., Chaurasia, S., Chiurchiù, S., Chowdhury, F., Cook, A. J., Cooper, B., Cressey, T.R., Criollo-Mora, E., Cunningham, M., Darboe, S., Day, N.P. J., De Luca, M., Dokova, K., Dramowski, A., Dunachie, S.J., Eckmanns, T., Eibach, D., Emami, A., Feasey, N., Fisher-Pearson, N., Forrest, K., Garrett, D., Gastmeier, P., Giref, A.Z., Greer, R.C., Gupta, V., Haller, S., Haselbeck, A., Hay, S.I., Holm, M., Hopkins, S., Iregbu, K.C., Jacobs, J., Jarovsky, D., Javanmardi, F., Khorana, M., Kissoon, N., Kobeissi, E., Kostyanev, T., Krapp, F., Krumkamp, R., Kumar, A., Kyu, H. H., Lim, C., Limmathurotsakul, D., Loftus, M.J., Lunn, M., Ma, J., Mturi, N., Munera-Huertas, T., Musicha, P., Mussi-Pinhata, M.M., Nakamura, T., Nanavati, R., Nangia, S., Newton, P., Ngoun, C., Novotney, A., Nwakanma, D., Obiero, C.W., Olivas-Martinez, A., Olliaro, P., Ooko, E., Ortiz-Brizuela, E., Peleg, A.Y., Perrone, C., Plakkal, N., Ponce-de-Leon, A., Raad, M., Ramdin, T., Riddell, A., Roberts, T., Robotham, J.V., Roca, A., Rudd, K.E., Russell, N., Schnall, J., Scott, J.A.G., Shivamallappa, M., Sifuentes-Osornio, J., Steenkeste, N., Stewardson, A.J., Stoeva, T., Tasak, N., Thaiprakong, A., Thwaites, G., Turner, C., Turner, P., van Doorn, H.R., Velaphi, S., Vongpradith, A., Vu, H., Walsh, T., Waner, S., Wangrangsimakul, T., Wozniak, T., Zheng, P., Sartorius, B., Lopez, A.D., Stergachis, A., Moore, C., Dolecek, C., Naghavi, M., 2022. Global burden of bacterial antimicrobial resistance in 2019: a systematic analysis. Lancet 399, 629–655.

Nava-Andrade, K., Carbajal-Arízaga, G.G., Obregón, S., Rodríguez-González, V., 2021. Layered double hydroxides and related hybrid materials for removal of pharmaceutical pollutants from water. J. Environ. Manag. 288, 112399.

Patel, M., Kumar, R., Kishor, K., Mlsna, T., Pittman, C.U., Mohan, D., 2019. Pharmaceuticals of emerging concern in aquatic systems: Chemistry, occurrence, effects, and removal methods. Chem. Rev. 119, 3510–3673.

Phelipe de Lima, D., Ferreira da Sliva, M., Ferreira da Sliva, A., Ide, A.H., Meili, L., 2020. In: EBA 13 - Brazilian Meeting on Adsorption. Fortaleza, Ceará, Brasil.

Renault, F., Morin-Crini, N., Gimbert, F., Badot, P.-M., Crini, G., 2008. Cationized starch-based material as a new ion-exchanger adsorbent for the removal of C.I. Acid Blue 25 from aqueous solutions. Bioresour. Technol. 99, 7573–7586.

Singha Roy, A., Kesavan Pillai, S., Ray, S.S., 2023. A comparison of nitrate Release from Zn/Al-, Mg/Al-, and Mg–Zn/Al layered double hydroxides and composite beads: utilization as slow-release fertilizers. ACS Omega 8, 8427–8440.

Trust, Wellcome, 2018. Initiatives for Addressing Antimicrobial Resistance in the Environment: Current Situation and Challenges. London.

UN General Assembly, 2015. Transforming Our World : the 2030 Agenda for Sustainable Development.

Vreysen, S., Maes, A., 2008. Adsorption mechanism of humic and fulvic acid onto Mg/Al layered double hydroxides. Appl. Clay Sci. 38, 237–249.

Wang, L., Shi, C., Wang, L., Pan, L., Zhang, X., Zou, J.-J., 2020. Rational design, synthesis, adsorption principles and applications of metal oxide adsorbents: a review. Nanoscale 12, 4790–4815.

Watkinson, A.J., Murby, E.J., Kolpin, D.W., Costanzo, S.D., 2009. The occurrence of antibiotics in an urban watershed: from wastewater to drinking water. Sci. Total Environ. 407, 2711–2723.

Wilkinson, J.L., Hooda, P.S., Barker, J., Barton, S., Swinden, J., 2016. Ecotoxic pharmaceuticals, personal care products, and other emerging contaminants: a review of environmental, receptor-mediated, developmental, and epigenetic toxicity with discussion of proposed toxicity to humans. Crit. Rev. Environ. Sci. Technol. 46, 336–381.

Williams, O., Clark, I., Gomes, R.L., Perehinec, T., Hobman, J.L., Stekel, D.J., Hyde, R., Dodds, C., Lester, E., 2019. Removal of copper from cattle footbath wastewater with layered double hydroxide adsorbents as a route to antimicrobial resistance mitigation on dairy farms. Sci. Total Environ. 655, 1139–1149.

World Health Organization, 2023. WHO Model List of Essential Medicines - 23rd List, 2023 (WHO/MHP/HPS/EML/2023.02).

Wu, F.-C., Tseng, R.-L., Juang, R.-S., 2009. Characteristics of Elovich equation used for the analysis of adsorption kinetics in dye-chitosan systems. Chem. Eng. J. 150, 366–373.

xing Zha, S., Zhou, Y., Jin, X., Chen, Z., 2013. The removal of amoxicillin from wastewater using organobentonite. J. Environ. Manag. 129, 569–576.

Yang, Z., Wang, F., Zhang, C., Zeng, G., Tan, X., Yu, Z., Zhong, Y., Wang, H., Cui, F., 2016. Utilization of LDH-based materials as potential adsorbents and photocatalysts for the decontamination of dyes wastewater: a review. RSC Adv. 6, 79415–79436.

Yang, C., Wang, L., Yu, Y., Wu, P., Wang, F., Liu, S., Luo, X., 2020. Highly efficient removal of amoxicillin from water by Mg-Al layered double hydroxide/cellulose nanocomposite beads synthesized through in-situ coprecipitation method. Int. J. Biol. Macromol. 149, 93–100.

Zaher, A., Taha, M., Farghali, A.A., Mahmoud, R.K., 2020. Zn/Fe LDH as a clay-like adsorbent for the removal of oxytetracycline from water: combining experimental results and molecular simulations to understand the removal mechanism. Environ. Sci. Pollut. Res. 27, 12256–12269.

Zhai, M., Fu, B., Zhai, Y., Wang, W., Maroney, A., Keller, A.A., Wang, H., Chovelon, J.-M., 2023. Simultaneous removal of pharmaceuticals and heavy metals from aqueous phase via adsorptive strategy: a critical review. Water Res. 236, 119924.

Zhang, J., Li, Y., Zhou, J., Chen, D., Qian, G., 2012. Chromium (VI) and zinc (II) waste water co-treatment by forming layered double hydroxides: mechanism discussion via two different processes and application in real plating water. J. Hazard Mater. 205–206, 111–117.