Journal of Environmental Chemical Engineering 9 (2021) 105197

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

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

# Understanding Layered Double Hydroxide properties as sorbent materials for removing organic pollutants from environmental waters

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 2RD, UK

ARTICLE INFO

Editor: Yunho Lee

*Keywords:*
Adsorption
Emerging contaminants
Layered Double Hydroxides
Methyl Orange
Organic pollutants
Wastewater treatment

## ABSTRACT

Emerging contaminants (ECs) are a group of anthropogenic organic pollutants known to have a host of adverse environmental and health implications. The removal of such pollutants from aqueous environments to ensure water is of a quality fit for reuse is therefore highly important and gaining considerable interest. Whilst there are multiple approaches used for EC remediation from water matrices, sorption using layered double hydroxides (LDHs) has been reported as a suitable technique. LDHs are interesting clay-like materials with numerous properties which lend LDHs to being suitable sorbent materials. Such properties include low toxicity, anion exchange capacity and tuneable structures through possible variations in metals, anions and preparation techniques. To design a successful sorbent material, it is important to fully understand the materials structure-property-function relationship. However, in the application of LDHs as sorbent materials for the removal of organic pollutants, this relationship is not well understood. Hence the ability to design bespoke high-performing LDH sorbent material is currently limited.

This review considers the impact of structure and related physiochemical properties of LDHs on their sorption capacity for the removal of organic pollutants from water matrices. Methyl Orange (MO) is first considered as a model pollutant, with the importance of the characteristics of the metal layers, interlayer anions and resulting textual properties of LDHs on reported sorption capacity observed. A comparison is then made between the findings from the MO case study and for the sorption of other organic pollutants using LDHs, with a particular focus on pharmaceuticals. Finally, the role of environmental conditions and considerations linked to possible commercial applications are discussed, with recommendations made for future work.

## 1. Introduction

The availability of clean and sanitary water is well recognised as being a key driver for sustainable development, highlighted in UN Sustainable Development Goal 6 [1]. However, it is widely reported that 80%, rising to 95% in some developing countries, of wastewater is released into the environment without any prior treatment [2]. Whilst there are a diverse range of pollutants found in wastewater a particularly concerning class of pollutants are emerging contaminants (ECs). Pollutants classified as ECs include numerous anthropogenic organic compounds, including synthetic hormones, pesticides, pharmaceuticals and personal care products (PPCPs), with many being associated with causing adverse effects on both human health and the environment [3]. Although such compounds are often present at low concentrations, ng/L to µg/L, in aqueous environments, they have been observed in a huge number of settings including in ground, surface, drinking and wastewater [3]. Further to this ECs can still have significant impacts on biological systems and ecosystems at these low concentrations, such as in the case of sub-inhibitory concentrations of antibiotics contributing to the spread of antimicrobial resistance [4].

ECs cannot be completely eliminated by conventional wastewater treatment processes therefore advanced techniques are required for their removal from aqueous environments. Advanced techniques deployed include, but are not limited to, advanced oxidation processes,

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*Abbreviations:* 2,4-D, 2,4-dichlorophenoxyacetic acid; BET, Brunauer-Emmett-Teller; CR, Congo red; DNOC, methyl-4,6-dinitrophenol; DNP, 2,4-dinitrophenol; EC, Emerging contaminant; LDH, Layered double hydroxide; LCA, Life cycle assessment; MO, Methyl Orange; PPCPs, Pharmaceuticals and personal care products; PZC, Point zero charge; SEM, Scanning electron microscopy; XRD, X-ray diffraction.

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

https://doi.org/10.1016/j.jece.2021.105197
Received 10 December 2020; Received in revised form 2 February 2021; Accepted 5 February 2021

constructed wetlands, adsorption, and filtration technologies [5,6]. Adsorption is a popular remediation technique as it is an effective and economical method, there is flexibility in design and operation, with the ability to develop a low energy separation strategy with low operational cost and remediation without toxic by-products, all in line with ideas of the circular economy [7]. If correctly designed the reversible nature of sorption processes can be harnessed, allowing for the recovery of the pollutant from the sorbent material, which in the case of valuable resources would be favourable. The shift to viewing pollutants in water streams as potential resources rather than a costly waste is closely linked to ideas of the circular economy, and in some cases such ideas are being built into water industry wide guidelines [8].

Sorbent materials that have been explored for the removal of ECs from aqueous environments include those commonly reported such as metal-organic frameworks [9] and activated carbons, including from low-cost precursors [10,11]. In addition novel solutions such as materials from waste plastics [12], graphene-based materials [13] and cyclodextrin-based sorbents [14] have been reported. Further to this anionic clay materials, Layered Double Hydroxides (LDHs), have also been utilised as sorbent materials. LDHs are an interesting class of sorbent materials, being relatively simple and typically low cost to synthesise, with properties including high surface area and anion exchange capabilities.

This review will consider the application of LDHs as sorbent materials for the removal of organic pollutants from aqueous environments. The focus is on understanding the characteristics of LDHs which make them successful sorbent materials, with the aim of identifying those properties which are the most important for the sorption of ECs. Following a short overview of LDHs, the sorption of a commonly used dye, Methyl Orange (MO), will be used as an initial case study to investigate the impact of the LDH structure on sorption properties. The findings of this case study will then be examined against the findings for the sorption of other organic pollutants, with the aim of aim of understanding if the property-function patterns observed for MO sorption are applicable more widely. A particular focus is paid to pharmaceuticals due to the increasing concern on their impact on the environment and involvement in the spread of antimicrobial resistance. Further to this the review will cover the impact of environmental conditions, before considering future commercial applications of LDHs as sorbent materials and making recommendations for future work.

## 2. Layered Double Hydroxides as sorbent materials

First discovered in the early 20th century, LDHs are a class of 2D anionic clays structurally similar to the naturally occurring mineral magnesium-aluminium hydroxyl carbonate [15]. LDHs are constructed from cationic metal containing layers and charge balancing hydrated anions in the interlayer space, with the general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2](A^{n-})_{x/n}\bullet mH_2O$. $M^{2+}$ and $M^{3+}$ are divalent and trivalent metal cations, x the molar ratio of the two metals and $A^{n-}$ a guest interlayer charge balancing anion. LDHs can be constructed from an array of divalent and trivalent metals, including but not limited to: $Mg^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $Al^{3+}$ and $Fe^{3+}$. A wide range different charge compensating anions can be intercalated into the LDH structure, including organic and inorganic species, the most commonly observed being halides (chlorides) and oxo-anions (carbonates, nitrates) [16]. The extensive combinations of both metals and anions which can be used to obtain LDHs result in a large class of isostructural materials, with varied and tuneable physiochemical properties. In this review $M^{2+}M^{3+}$-$A^{-}$-LDH will be used to display LDH composition, in the instances where the nature of the anion is not clear, or relevant for the discussion, it is omitted.

The range of different synthesis techniques employed in the preparation of LDHs (Fig. 1) have been covered in detail in several recent reviews, and hence will not be discussed in detail in this review [18–20]. It is recognised that the chosen synthesis technique may impact the final properties of an LDH and hence their suitability for their chosen final application [19,21]. Arguably the most commonly used synthesis technique for the preparation of LDHs is through a coprecipitation method, and whilst this is a simple widely applied technique there are a number of drawbacks, including difficulties in producing consistent particle size and distribution of LDH, hence other techniques are gaining interest in the literature [22].

The combination of unique properties LDHs possess have led to their exploitation in various applications, and whilst a full discussion is not included in this review some applications are shown in Fig. 1. Their relatively high surface areas, up to around 200 $m^2/g$, possible porosity and anion exchange capacity through the mobility of the interlayer

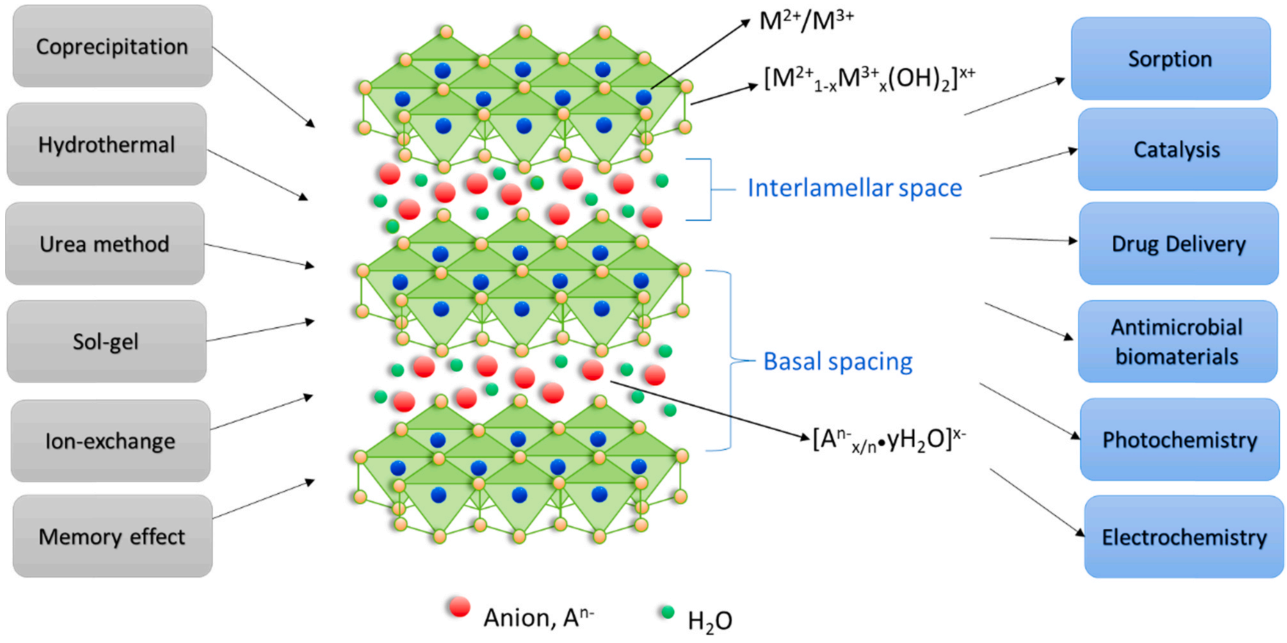

**Fig. 1.** Diagram showing the synthesis methods, structure and applications of Layered Double Hydroxides, Adapted from Mishra et al. [17].

anions, has led to the application of LDH as sorbent materials [23]. LDHs have been used as sorbent materials for a wide range of different pollutants from aqueous environments, ranging from oxyanions [24], phosphate [25], metals [26], radioactive materials and Uranium [27,28] through to organic pollutants such as dyes [29,30], pesticides [31,32], herbicides [33] and PPCPs [34]. The latter collection of organic pollutants has been somewhat less reviewed in the literature and is the focus for this review.

Another property which has been exploited in the application of LDHs as sorbent materials is the so called memory effect, in which LDHs can be calcined at around 500 °C to form the associated metal oxides, which on exposure to an aqueous environment reform the original LDH layered structure [35,36]. As the mechanisms for sorption for such materials differ from those present in uncalcined LDHs calcined LDHs are not included in this review. There is also a concern about how applicable a reconstruction technique may be for any large-scale applications of LDHs as sorbent materials [21]. It should also be mentioned that there are also a wide range of hybrid and composite materials including LDHs being utilised for water remediation, which although another interesting body of research is outside the scope of this review [37,38].

It is often reported that the properties of LDHs including the facile manipulation of adsorbent sites at the atomic scale and the ability to control the morphology and pore structure are key in being able to tune active sites for high performing adsorbent materials (Li, 2014) [91]. However, to be able to harness the possibilities of using LDHs as sorbent materials a deeper understanding of the fundamental relationship between physiochemical properties and sorption capacity is required. There are few studies which aim to understand how LDH properties influence the sorption of organic pollutants, nor on how such knowledge can be translated from one class of pollutants to another. Being able to better understand such structure-activity relationships would allow for the design of more effective sorbent materials.

## 3. Methyl Orange sorption as a case study for LDH sorption of organic pollutants

MO is a water-soluble azo dye commonly used in industry and research, however as it is a known carcinogen and has an adverse impact on the environment, its removal from the environmental is important [39]. MO has been chosen as a model case study pollutant in this review due to the large number of studies which have considered its removal from aqueous environments, allowing for a comprehensive exploration of the role of LDH properties on their sorption capacity for the removal of one pollutant [29].

There are a wide range of different LDHs which have been used for the sorption of MO (Table 1), which differ in both their composition and preparation technique, resulting a range of reported maximum sorption capacities of between 50 mg/g and over 1000 mg/g. The majority of studies are well described by the Langmuir isotherm and pseudo-second order kinetic model, in agreement with the finding of Yang et al. in their 2016 review of the sorption of dyes using LDHs. Sorption isotherms are used to predict the amount of sorbate which can be adsorbed on to a surface at equilibrium, with the Langmuir isotherm based on several assumptions, including a fixed number of identical adsorption sites, sorption occurs on a monolayer and no interactions between adsorbed molecules [56]. The kinetics describe the rate of sorption, with the pseudo-second order model often found to represent chemisorption processes such as ion exchange processes, and has been widely applied for the adsorption of pollutants from aqueous solutions [57]. Whilst firm conclusions cannot be made about sorption mechanism from isotherm or kinetic models the consistency in findings indicate possible similarities between the sorption process taking place [58].

The two most common mechanisms reported for organic pollutant sorption by LDHs are external surface sorption and interlayer anion exchange. Anion exchange is a result of the replacement of the interlayer anion with anionic pollutants present in the surrounding aqueous environment, and can be observed through shifts in the *003* reflections in X-Ray Diffraction (XRD) pattern resulting from increases in the basal spacing [49]. The anion exchange capacity of the LDH is dependent on a number of different factors, including cationic metal ratios, ability of the interlayer anion to stabilise the layers and the molecular mass of both the cations and anions present in the LDH [19]. Surface sorption takes place primarily through electrostatic interactions between positively charged external surfaces of LDHs and anionic pollutants [59]. In most instance, it is seen that the materials with high sorption capacities have anion exchange capabilities as well as surface sorption (Table).

Studies have explored the anion exchange mechanism in more detail, primarily through the observation of an XRD pattern of the LDH post-MO sorption. The post-sorption XRD of a NiAl-LDH showed three distinct peaks at the *003* position, rather than one peak in the pre-sorption XRD pattern, explained by envisaging an “intercalation-split mechanism”, an expansion of the interlayer spacing with the MO, followed by a compression of the adjacent interlayer spaces [46]. This was also found for the sorption of MO on to CoAl-LDH [41]. Similarly, the possible contraction of adjacent layers following sorption through changes in the XRD *003* plane was observed for the sorption of MO onto MgAl-LDH, however, this was not observed for the sorption of other dyes in the same study, which highlights potential differences in mechanism depending on the pollutant in question [47].

### 3.1. Role of interlayer anions in sorption capacity

The availability of the anion exchange mechanism is impacted by the nature of the interlayer anion of the LDH. There is a well reported hierarchy of anion exchange preference of different anions, depending on the charge density of the anion and the resulting strength of interaction with the metal layers of the LDH, reported as: $NO_3^- < Br^- < Cl^- < OH^- < SO_4^{2-} < HPO_4^{2-} < CO_3^{2-}$. Carbonate ions, which have the highest charge density, have the strongest interaction with the metal layers of the LDH reducing the possibility of anion exchange, with even small amounts of carbonate influencing sorption processes [23,60]. A number of the MO sorption studies with no anion exchange reported, such as onto ZnMgAl-LDH and NiAl-LDH, are materials which reported having large amounts of interlayer carbonate present [42,55]. The presence of different anions ($Cl^-$, $NO_3^-$, $SO_4^{2-}$ and $CO_3^{2-}$) on the sorption capacity of NiFe-LDHs was also investigated, reporting the lowest removal percentage for the $CO_3$-LDHs, reaching a maximum of around 40% compared to greater than 90% for Cl- and $NO_3$-LDHs [43].

Carbonate contamination resulting from the preparation method used for the LDH synthesis has also been shown to impact sorption capacity. As reported by Chen et al. [35] the difference in sorption capacity of two CoAl-Cl-LDH (801.1 mg/g against 324.4 mg/g) was explained through the use of a novel acid salt treatment over a traditional coprecipitation method which lead to a reduction in carbonate contamination. Further to this both Cl-LDHs had a higher sorption capacity than the directly synthesised $CO_3$-LDH, recording a sorption capacity of 49.8 mg/g [41].

### 3.2. Role of metals in sorption capacity

The metals used in LDHs can be varied through the combination of different metal precursors used and the corresponding ratio of M(II) to M(III) species in the metal layers. There are numerous examples of different combinations of metals in LDHs utilised for MO sorption (Table 1) with no obvious clear preference relating back to the sorption capacity of the materials for MO. However, metals present in the LDH have been reported to affect textual properties of the materials which could be impacting sorption capacity, including a change in interlayer free space and pore characteristics [61]. Few studies have directly compared the impact of different metals on LDH sorption for MO, and due to the difference in the synthesis methods used in various studies it is

**Table 1**
Summary of the removal of Methyl Orange by Layered Double Hydroxides.

| LDH material | Molar ratio ($M^{2+}$/ $M^{3+}$) | LDH synthesis technique; morphology (if reported and of note) | Specific surface area ($m^2$/ g) | Adsorbate dose (g/L) | pH | Temp (K) | $Q_{max}$ (mg/g) | Isotherm | Kinetics | Adsorption mechanism | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|
| MgAl-$NO_3$-LDH | 2:1 | Hydrothermal | NA | NA | 6.5 | 298 | 148 | Langmuir; Freundlich | 2nd | Surface sorption | [40] |
| CoAl-Cl-LDH | 4:1 | Hydrothermal followed by acid-salt treatment | 26.5 | 80–240 | 7 | 298 | 801.08 | Langmuir | 2nd | Anion ion exchange (expansion-extrusion mechanism) | [41] |
| CoAl-Cl-LDH | 4:1 | Coprecipitation | 30.90 | 80–240 | 7 | 298 | 329.42 | Langmuir | 2nd | NA | [41] |
| CoAl-$CO_s$-LDH | 4:1 | Hydrothermal | 19.7 | 80–240 | 7 | 298 | 49.84 | Langmuir | 2nd | NA | [41] |
| MgAl-$NO_3$-LDH | 2:1 | Coprecipitation | NA | 6–1637 | NA | 298 | 1800 | – | 2nd | Anion exchange; surface sorption | [68] |
| NiAl-$CO_3$-LDH | 1:1 | Dilute coprecipitation; flower-like | 133.00 | 50–200 | NA | 298 | 500.6 | Langmuir | 2nd | Surface sorption | [42] |
| NiAl-$CO_3$-LDH | 1:1 | Conventional coprecipitation | 90.00 | 50–200 | NA | 298 | 291.9 | Langmuir | 2nd | NA | [42] |
| NiFe-Cl-LDH | 4:1 | Coprecipitation | 36.98 | 80 | 5.5 | 303–333 | 769.2 | Langmuir | 2nd | Anion exchange; Surface sorption | [43] |
| NiCo-$NO_3$-LDH | 1:1 | Hydrothermal; 3D flower-like | 37.00 | 20–200 | 7 | 298 | 497 | Langmuir | 2nd | Anion exchange; surface sorption | [44] |
| NiFe-$CO_3$-LDH | 2:1 | Low temperature coprecipitation | 427.00 | 50–300 | 7 | RT | 426 | Langmuir | 2nd | Anion exchange; surface sorption through hydrogen bonding, electrostatic interaction | [45] |
| NiAl-Cl-LDH | 4:1 | Hydrothermal followed by acid-salt treatment | 30.65 | 20–200 | 7 | 298 | 853.19 | Langmuir | 2nd | Anion exchange (Intercalation-split mechanism) | [46] |
| NiAl-Cl-LDH | 4:1 | Coprecipitation | 95.44 | 20–200 | 7 | 298 | 290.1 | Langmuir | 2nd | NA | [46] |
| NiAl-$CO_3$-LDH | 4:1 | Hydrothermal | 13.00 | 20–200 | 7 | 298 | 138 | Langmuir | 2nd | NA | [46] |
| MgAl-Cl-LDH | 2:1 | Hydrothermal using deep eutectic solvents; microspheres | 26.64 | 200 | 7 | 298 | 1030.13 | Langmuir | 2nd | Surface sorption; anion exchange (including contraction of adjacent layers) | [47] |
| MgAl-Cl-LDH | 1:1 | Hydrothermal using deep eutectic solvent; microspheres | NA | 100–600 | 7 | 298 | 922.23 | NA | NA | NA | [47] |
| ZnAl-Cl-LDH | 2:1 | Coprecipitation with urea; microspheres | 253.00 | 10–300 | NA | RT | 523 | NA | NA | NA | [48] |
| CoFe-$NO_3$-LDH | 4:1 | Coprecipitation | 108.84 | 5–300 | 7 | 298 | 1206 | Langmuir | 2nd | Surface sorption; anion exchange | [49] |
| NiFe-$NO_3$-LDH | 4:1 | Coprecipitation | 17.84 | 10–180 | NA | RT | 205.76 | Langmuir | 2nd | Surface sorption; anion exchange | 50] |
| MgAl-Cl-LDH | 3:1 | Not reported – from a commercial source | NA | < 1636 | NA | RT | 948 | Freundlich | NA | NA | [51] |
| ZnAl-Cl-LDH | 2:1 | Coprecipitation | NA | < 1636 | NA | RT | 948 | Freundlich | NA | NA | [51] |
| ZnAl-Cl-LDH | 3:1 | Coprecipitation | NA | < 1636 | NA | RT | 752 | Freundlich | NA | NA | [51] |
| ZnAl-Cl-LDH | 4:1 | Coprecipitation | NA | < 1636 | NA | RT | 1406 | Freundlich | NA | NA | [51] |
| CoCu-$NO_3$-LDH | – | Ultrasonication from ZIF-67 (MOF) precursor | 29.33 | 200 | NA | 298 | 1063.8 | Freundlich | 2nd | Electrostatic interactions | [52] |
| MgFe-Cl-LDH | 2:1 | Solvothermal with SDS; petal-like | 70.19 | 50–200 | 4 | 298 | 534 | Langmuir | 2nd | Anion exchange | [53] |
| MgNiAl-$CO_3$-LDH | 2:1 | Coprecipitation | 137.40 | 10–500 | 8 | 298 | 118.5 | Langmuir | 2nd | NA | [54] |
|  |  | Coprecipitation | 28.12 | 10–100 | 3 | RT | 883 | Langmuir | 2nd | Surface sorption | [55] |

(continued on next page)

**Table 1** (*continued*)

| LDH material | Molar ratio ($M^{2+}$/ $M^{3+}$) | LDH synthesis technique; morphology (if reported and of note) | Specific surface area ($m^2$/g) | Adsorbate dose (g/L) | pH | Temp (K) | $Q_{max}$ (mg/g) | Isotherm | Kinetics | Adsorption mechanism | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|
| ZnMg-Al-$CO_3$-LDH | 2:1(Zn/ Mg ratio 0.125) | | | | | | | | | | |
| ZnMg-Al-$CO_3$-LDH | 2:1 (Zn/ Mg ratio 0) | Coprecipitation | 28.12 | 10–100 | 3 | RT | 577.5 | Langmuir | 2nd | Surface sorption | [55] |
| ZnMg-Al-$CO_3$-LDH | 2.1 (Zn/ Mg ratio 0.5) | Coprecipitation | 43.92 | 10–100 | 3 | RT | 403.2 | Langmuir | 2nd | Surface sorption | [55] |
| ZnMg-Al-$CO_3$-LDH | 2.1 (Zn/ Mg ratio 0.8) | Coprecipitation | 22.65 | 10–100 | 3 | RT | 315.4 | Langmuir | 2nd | Surface sorption | [55] |

*Notes*: NA = not available; RT=Room Temperature; kinetics 2nd = pseudo-second order; $Q_{max}$ = maximum sorption capacity

difficult to make broader comparisons to understand the role of different metals on the sorption capacity of LDHs. There is clear space for more comparative studies to help understand the role the metals used in the LDH are having on sorption properties.

The impact of varying the ratio of divalent to trivalent metal species in the LDH, and subsequent variation in charge density of the metal layers, has been more widely studied. Two similar studies investigated the impact of the ratio of M(II) and M(III) ions in the metal layers for CoAl- and NiAl-LDH. In both cases the highest sorption capacity is observed for the materials with higher proportion of M(II), with $M^{2+}{}_4Al_1$-LDH giving sorption capacities of 827.5 mg/g and 909.8 mg/g respectively whilst the $M^{2+}{}_2Al_1$-LDH giving sorption capacities of 581.9 mg/g and 749.4 mg/g. This is attributed to the increase in the interlayer spacing and the decrease in surface area per unit charge resulting from the percentage decrease in $Al^{3+}$, allowing for greater ease in anion exchange through improved anion mobility [41,46]. A similar trend was observed for CoFe-LDHs with a sorption capacity of 1290 mg/g for the 4:1 ratio compared to 93–135 mg/g for lower ratios, and further to this the sorption capacity for MgAl-LDH was found to follow the same trend, 922.23 mg/g for the 1:1 ratio compared to 1051.87 mg/g for the 2:1 ratio [47,49]. The authors of the CoFe-LDH study also include an explanation including the influence of pore structure of the difference in sorption capacities, discussed in the next section of this review, however the decrease in layer charge is also likely to play a role [49].

The opposite trend is seen for studies which do not report anion exchange as a sorption method. A study exploring ZnAl-LDHs found the following sorption capacities, $Zn_2Al$-LDH (2.9 mmol/g); $Zn_3Al$-LDH (2.9 mmol/g); $Zn_4Al$-LDH (2.3 mmol/g), showing the smaller Zn:Al ratios resulted in higher sorption capacities for MO. Due to carbonate contamination resulting from the synthesis method used in this study, a greater charge density of metal layers is likely to promote surface sorption though electrostatic interactions overriding the impact of decreasing ease of anion exchange, resulting in higher sorption capacities [51]. For NiFe-$CO_3$-LDHs, the 2:1 ratio was found to have the highest sorption capacity, 426 mg/g, however this was not discussed in detail by the authors [45]. Whist anion exchange was considered as a sorption mechanism in this study very little analytical data was provided to support this claim beyond a very small change in the XRD pattern following sorption, and the presence of carbonate would make the occurrence of anion exchange unlikely, so surface sorption including electrostatic interactions is the most likely the dominant sorption mechanism.

### 3.3. *Implication of 3D structure of LDHs on sorption capacity*

The sorption capacity of a material is highly impacted by physical properties, such as surface area, porosity and pore diameter [62]. Whilst surface area is often cited as being key in determining the properties of LDHs, the data presented in Fig. 2 it can see there is not a simple linear correlation between specific surface area and sorption capacity. Similar observations have been made by Chubar et al. [21], and they also highlighted that even when a surface area to sorption capacity observation correlation is observed the dependency is not proportional.

The complex relationship between surface area and sorption capacity is replicated in individual studies, for example NiCo-LDHs synthesised with varying metal ratios (from 4:1 to 1:4) did not show a clear correlation between the sorption capacity for MO and the Brunauer-Emmett-Teller (BET) surface area. The $Ni_1Co_1$-LDH, specific surface area of 37 $m^2$/g, showed the highest sorption capacity, whereas other materials with higher specific surface areas showed much lower sorption capacities (e.g. $Ni_1Co_3$-LDH has a specific surface area of 120 $m^2$/g). This is explained by the synergistic effects of the anion exchange and the surface based adsorption mechanisms, and as discussed earlier in the review the changes in metal ratios will impact these two mechanisms in different ways due to the role metal layer charge density has [44]. It is worth mentioning in this study little data is presented about any of the other materials beyond the highest performing $Ni_1Co_1$-LDH. However, researchers are still assuming surface area to be the key differentiating property between LDHs in regards to their different sorption capacities, for example the improved sorption capacity of MgAl- against ZnAl-LDHs (4.3 mmol/g against 2.9 mmol/g) was put down to the MgAl-LDH having a higher surface area, however this study did not report BET surface areas, only putting an increased specific surface area down to scanning electron microscopy (SEM) imaging observations and comparison of the full width at half-maximum of the *003* reflections in the XRD patterns [51]. With the lack of further physiochemical properties reported in the study it makes it difficult to conclude that there are no other properties which may have arisen from the likely differences in

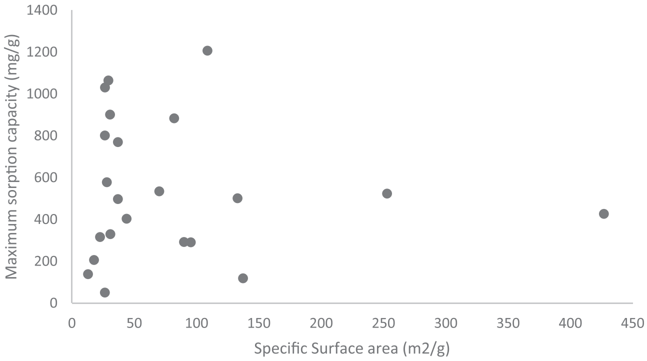

**Fig. 2.** Relationship between specific area of LDHs against maximum sorption capacity of MO reported. Data displayed in Table 1.

synthesis technique which may have impacted the sorption capacity. Other studies have shown a positive relationship between surface area and increased sorption capacity, such as for NiFe-LDH synthesised at low temperature, attributed to having a higher specific surface area compared to similar LDH analogues synthesised at higher temperatures (427 $m^2/g$ compared to 199 $m^2/g$), although the two materials also showed quite varied pore size distributions which could also be contributed to the observed sorption capacities [45].

LDH pore characteristics, including average pore diameter, presence of micro- and meso-porosity and pore volume are also shown to play a role in sorption capacity for MO. LDHs are typically reported as having a Type IV isotherm and a H3 hysteresis, corresponding to slit like pores in the secondary particles of aggregated nanosheets of LDH [63], reported in a number of the LDH MO sorption studies [42,47,53,64]. However, there are some exceptions to these broadly consistent findings, with LDHs showing differing isotherms and hysteresis. CoFe-LDH, with varying metal ratios, appear to show H4 hysteresis characteristics, indicating both micro- and meso- porosity [49]. This study is one of the few to highlight that the reason for higher sorption capacity of the $Co_4Fe$-LDH to those with lower Ni:Fe ratios could be attributed to different in pore sizes. The authors discuss the importance of pore diameters to be greater than 4.2 nm for the transport of MO, which has a size of around 1.4 nm [49]. Another study which highlights the importance of pore size is the study of CoCu-LDH synthesised from ZIF-67, in which the CoCu-LDH has a much higher sorption capacity than the starting precursor (1063.8 mg/g against approx. 50 mg/g). This change in sorption capacity can somewhat be explained through the increase of pore size from 1.54 nm to 26.94 nm which allowed for increased MO interactions and improved diffusion of the MO through the particles. This increase in pore size was not accompanied by an increase in surface area, with the reverse being observed for surface area, which decreased from 1138.7 $m^2/g$ to 29.3 $m^2/g$ [52].

The interlayer anion of the LDH also appears to impact the pore characteristics, and whilst in a study of different anions within NiFe-LDH were all described as having Type IV isotherm and H3 hysteresis when taking a closer look at the data reported the $N_2$ adsorption-desorption curves look to be closer to a H2 hysteresis [43]. This is supported by a Type IV isotherm with a H2 hysteresis for an NiFe-LDH being reported in a separate study [50]. With the difference in sorption performance seen with the different interlayer anions within LDHs with the same metals, there could be a possibility that this role in influencing pore structure could be contributing to the sorption performance, although not something which is widely discussed in the literature. Beyond the interlayer anion both the pore size distribution and pore size are related to the preparation method employed and the choice of metal cations in the LDH synthesis [23].

Surface area and pore structure of LDHs are intrinsically linked to the hierarchical 3D structure of LDH particles. 3D-hierarchical nanostructures of LDHs have gained attention due to the fact they appear to have greater performance in multiple applications, and in attributed to the fact that they can have a higher surface area and unique pore structure when compared with 2D analogues [65]. Whilst most LDHs are most often found to be distinct platelet like particles, some studies do show LDHs with differing particle morphology impacting the sorption capacity of the LDH for MO. A NiAl-LDH with a flower-like morphology was found to have a higher sorption capacity for MO than a conventional NiAl-LDH, with a sorption capacity of 500 mg/g against 292 mg/g. The authors put the differences in the sorption capacity down to the higher surface area, pore volume and the pore sizes [42]. Differences in the crystallinity of the particles was also observed resulting from the different synthesis techniques utilised, with the conventional LDH showing smaller peaks in the XRD pattern as a result of the highly aggregated large LDH particles, backed up by the SEM analysis. Guan et al. [44] studied flower-like hierarchical NiCo LDH structures, which showed a relatively high sorption capacity for MO, 497 mg/g. 3D-hierarchical microspheres of ZnAl-LDHs, with a core-shell structure, also showed good sorption characteristics (523 mg/g), and this was explained through an improved structure with a suitable mesoporous distribution as a result of the morphology of the particles [48]. It is important to highlight that neither of the final two studies discussed include a direct comparison to LDH of the same composition which lack a 3D structure. The characteristics and ratio of metals present in the LDH has also been shown to impact the final 3D-structure, for example in a ZnMgAl-LDHs when the concentration of Zn was increased the integrity of the blossom sphere morphology observed decreased, observed through SEM images, with the Zn/Mg= 0.125 ratio LDH showing the greatest sorption capacity and most defined blossom sphere morphologies [55].

## 4. Translating LDH for Methyl Orange removal to wider organic pollutants

Whilst there are numerous studies reporting the removal of MO using LDHs, and some conclusions can be drawn about the sorption properties for this pollutant there are of course a much more diverse array of pollutants present in the environment which need to be removed. For this reason it is important to understand if the same LDH properties are important for the sorption of other organic pollutants to allow for effective design of LDH sorbent materials for a wider array of arguably more concerning pollutants. For example, pharmaceuticals are one class of ECs which their presence in the environment is becoming ever more concerning, and whilst there is literature showing that sorption is a suitable remediation technique [66] to progress research in this area it is important to know if finding from studies carried out on previously more common pollutants can be translated to the removal of pharmaceuticals. Ideally when making such comparisons, studies should be carried out which look at the removal of an EC of interest, alongside a more commonly studied pollutant, using the same sorbent material under the same experimental conditions, however even in studies where this has been highlighted as an important area of research only one or two lines of the article have been dedicated to the sorption of the pharmaceutical [45]. Therefore, in this section a broader approach is taken, to understand if the overarching patterns observed from MO sorption studies can be translated to the sorption of other ECs.

There are a number of differing studies which have looked at the sorption of different organic pollutants, including dyes, pharmaceuticals and pesticides, by LDHs (Table S.1). Before discussing the findings regarding the properties and characteristics of the LDHs it is important to consider the diversity of structures within the organic pollutants presented. Properties of the pollutant such as the charge, functional group and solubility may impact the sorption capacities which are reported for each pollutant, and therefore it might not be possible to compare the absolute sorption capacities between different pollutants. In the most extreme example, no sorption will be observed for removing certain pollutants from the water phase. This is the case for sorption of pharmaceuticals onto MgAl-LDH, in which sorption was observed for tetracycline and diclofenac, whereas no sorption was observed for chloramphenicol [34]. This is due to the cationic nature of chloramphenicol in aqueous environments, resulting in no electrostatic interactions or anion exchange being possible.

The number of functional groups and associated charge on the organic pollutant can also impact sorption through differing number of active sorption sites being occupied, and the cross sectional area of the species can impact the sterics of the sorption process also playing a role in overall sorption capacity [67,68]. The variation in sorption capacity is not always discussed in detail which can lead to difficulties in understanding the impact of different properties of the pollutant on the observed sorption capacity, for example no explanation is made for the differences in sorption capacity observed for three different red dyes on to a MgAl-LDH [69]. Finally, and important for the comparisons back to MO as a model pollutant, as highlighted by Darmograi et al. [68] MO shows a much higher sorption capacity than other orange dyes investigated (5.5 mmol/g compared to 2.7 and 1.7 mmol/g) due to MO having smaller cross-sectional area and a single sulfonate functional group. Hence, sorption capacities observed for organic pollutants which are larger than MO possessing a greater number of functional groups may not display such high maximum sorption capacities as those observed for MO sorption. For this reason, no direct comparisons to specific sorption capacities between MO and other pollutants are made in this review, and the focus is on general trends in LDH structure.

### 4.1. Focus on pharmaceuticals as pollutants

Pharmaceuticals are a diverse class of compounds which have been widely detected in aqueous environments across the globe [70]. As pollutants in the environment the presence of pharmaceuticals is known to being have both long- and short-term impacts, including negative impacts on aquatic organisms [71] and contributing to the spread of antimicrobial resistance [72,73]. Due the emerging nature of pharmaceuticals as environmental pollutants they are not as widely studied as other pollutants such as organic dyes, however due to their clear consequences on the environment and human health there is a need to investigate their removal from water matrices [74].

As seen for MO sorption many of the studies reported are well described by the Langmuir isotherm and pseudo-second order kinetics (Table S.1). There are exceptions, such as the sorption of metronidazole onto MgAl-LDHs being best described by the Sips isotherm, an isotherm which combines both the common Langmuir and Freundlich isotherms depending on the initial sorbate concentration [75]. The Sips isotherm has also been observed in other studies including the sorption of *o*-nitrophenol on to various $M^{2+}$Al-LDH [76]. The Freundlich isotherm is also found to be the best fitting for some studies, including the sorption of norfloxacin onto MgAl-LDH [77].

Clear parallels are seen to the MO sorption regarding the importance of the anion exchange mechanism. Although much smaller sorption capacities are observed, the sorption of norfloxacin onto MgAl-LDHs, the Cl-LDH was found to have a higher sorption capacity compared to the $CO_3$-LDH due to the anion exchange mechanism only being observed for the Cl analogue [77].

The impact of different metals used in LDH synthesis has been explored, with several findings like those seen in the MO case study examples. A study investigating the sorption of oxytetracycline highlights the impact the metals present within the LDH can have on the impact of the sorption capacity, with the following sorption capacities reported: CuAl-LDH, 109.0 mg/g; MnAl-LDH, 23.1 mg/g; CuMnAl-LDH, 156.9 mg/g. However, the reasons behind these differences are not well discussed though data regarding the physiochemical properties of the LDHs reported, but SEM images indicate different particle morphology which has been highlighted in MO studies as a contributing factors to differences in sorption capacity [78]. Worth highlighting is that different metal salts were used in the synthesis, so it is unclear what the characteristics of the anions are in each LDH and how this differs between the LDHs and the potential role this may be having on sorption capacity.

Moaty et al. [79] also investigated the impact of different metals comparing MgAl- and MgFe-LDH on the sorption of doxycycline. Primarily, similar to a number of MO sorption studies, the hypothesis that surface area of an LDH is not the key property behind improved sorption capacity is backed up, as the MgFe-LDH has a surface area of 101.6 $m^2$/g whilst the MgAl-LDH only has a surface area of 4 $m^2$/g whereas the sorption capacities recorded are 71.6 mg/g and 100 mg/g respectively. The authors of this study put the improved sorption capacity of the Al-based LDH down to the differences in zeta potential of the two LDHs, with the Fe-based LDH having a zeta-potential of −17.8, which would result in electrostatic repulsion of the anionic form of the pharmaceutical, hence decreasing the surface sorption on to the LDH, opposite to the MgAl-LDH which has a positive zeta potential of 26.6 [79]. However, a negative zeta potential is an unusual observation [80], and if this was the case there would be total electrostatic repulsion resulting in very little sorption which is not the case in this study as a sorption capacity of 71.6 mg/g is still observed. For example, no sorption of chloramphenicol was observed on to MgAl-LDH, as it was present in cationic form in solution, resulting in electrostatic repulsion with the positively charge LDH surface [34]. It has also been reported that zeta potential of LDHs, whist an interesting property, has no correlation to sorption performance [21]. Not discussed by Moaty et al. [79] is the impact of the difference of pore structures or $N_2$ adsorption-desorption isotherms observed which could be playing a role as differences have been seen in previously discussed studies.

Overall, whilst there are only a relatively small number of comprehensive studies which have explored the sorption of pharmaceuticals on to LDH materials, the patterns emerging are similar to those seen for MO sorption. In the next section the scope of the pollutants in expanded to consider if the findings are in line with the sorption of other organic pollutants beyond pharmaceuticals.

### 4.2. Applications beyond pharmaceutical pollutants

Congo Red (CR) is an anionic azo dye with similar properties to MO. As discussed with MO studies the material which shows the highest sorption of CR at 909.2 mg/g is a hierarchical porous NiCo-$NO_3$-LDH, with both anion exchange and electrostatic interactions observed as the sorption mechanism [81]. The importance of the 3D morphology of the LDH particle, the pore structure and surface area is observed in further studies, including the sorption capacity of 521.2 mg/g observed for CR sorption on to a NiCo-LDH structure described by the authors as a nanoflower lantern, which was observed to have a hierarchically porous structure, with specific surface area of 214.28 $m^2$/g and pore diameters distribution of 4.2–159.3 nm [82]. Again showing parallels to the findings of the MO sorption studies the materials which showed lower sorption capacities for CR (111 mg/g on to a MgAl-LDH) were found to have carbonate contamination in the interlayer resulting in no anion exchange [83]. Moving away from CR studies, the importance on the anion exchange mechanism for improved sorption capacity is also seen for the sorption of two dinitrophenol pesticides, 2,4-dinitrophenol (DNP) and methyl-4,6-dinitrophenol (DNOC), on to MgAl-LDH, with the Cl-LDH showing higher sorption capacity than the carbonate based analogue [31].

Highlighting the needed to consider physiochemical properties resulting from the inclusion of different metals into the LDH is show through a study investigating the sorption of Reactive Red dye onto NiAl-, MgAl- and CoAl-LDH, which found that the Ni-based LDH showed the highest sorption capacity (5.04 mg/mmol). This was attributed to the improved morphology of the particles in the Ni-LDH which showed a higher surface area and broader interlayer space (64.7 $m^2$/g and 7.81 Å compared to 27.5 $m^2$/g / 12.9 $m^2$/g and 7.75 Å / 7.66 Å for the Mg-and Co-based LDHs respectively which showed sorption capacities of 4.16 and 2.33 mg/mmol) [84]. The metal ratio of Ni/Al in this LDH was greater than the M(II)/M(III) ratio than seen in the other LDHs (3.2 compared to 2.88 and 2.70 respectively for the others), impacting the charge density, which may be playing a role in the difference in sorption capacity. The impact of different metals in LDHs on the sorption of fumonisin-$B_1$ has also been studied, with the overarching findings showing that MgFe-LDHs, both with chloride and nitrate interlayer anions, have lower sorption capacity than MgAl-LDH analogues [85]. No data on physiochemical properties of the LDHs are presented in the study beyond microscopic observations indicating that there were no differences between the materials, hence it is difficult to draw any conclusions about which properties the inclusion of Fe over Al in the LDH structure is making. As in the MO studies, the impact the ratio of metals and associated different in layer charge has been reported for other pollutants, such as the sorption of DNP and DNOC on to MgAl-LDH, with the maximum sorption capacity seen for Mg/Al ratio of 3 (4.89 mmol/g and 2.54 mmol/g respectively) [31].

One additional area of research not discussed in MO or pharmaceutical sorption is the possible influence of the orientation of interlayer anions on anion exchange mechanisms. A 2007 study shows the impact that the ratio of metals in the MgAl- LDH impacts the orientation of the nitrate anion in the interlayer [86]. Subsequently it has been observed in a study of the influence of metal ratios on the sorption capacity of MgAl-LDHs for 2,4-dichlorophenoxyacetic acid (2,4-D), that the change in metal ratio and hence change in nitrate orientation may impact the possibility of anion exchange [59]. It was found that a LDH with a Mg/Al ratio of 7/2 has a lower sorption capacity and no observable anion exchange, whereas the LDH with a 2/1 Mg/Al ratio has a higher sorption capacity, and this was put down to the perpendicular orientation of nitrate interlayer anions in the latter LDH allowing for anion exchange to take place which was not possible for the former LDH. This is not something which have been considered in other studies, so is an area where more attention could be paid in the future.

## 5. Environmental factors affecting organic pollutant sorption on to Layered Double Hydroxides

Due to the nature of sorption process a wide range of environmental parameters influence sorption capacity, hence the impact of operational environmental conditions needed to be considered whilst designing sorbent materials.

### 5.1. Role of pH

pH has great influence on adsorption processes and sorption capacity, especially when electrostatic interactions are involved, due to role in varying charge on functional groups of the pollutant and the surface of the LDH. The impact of pH is illustrated by the sorption of sunset yellow dye on to a CaAl-LDH, with the sorption capacity, which the maximum sorption capacity peaks at pH 4. Below the pH of the point zero charge (PZC) of the LDH surface (pH 7 for CaAl-LDH) the surface of the LDH is negatively charged, which results in both of the sorption mechanisms being less effective as electrostatic interactions between the anionic pollutant and the charged surface can no longer take place, and the anion exchange of the pollutant has to compete with free hydroxy radicals [87]. The sorption capacity decreases when the pH is below 4 due to the dissolution of the LDH, which is seen in multiple studies, such as the limits of pH 4 and pH 10 seen for the sorption of MO onto NiMgAl-LDH [54]. A slightly different pattern is observed in the case of the sorption of MO onto NiAl-LDH, both flower-like and conventional morphology, in which the removal efficiency is highest at acidic pH (3−5) decreasing as the pH becomes more basic, up to pH 11, which is put down to the enhanced electrostatic interactions between the LDH and sorbents at acidic pH and enhanced stability of Ni containing LDHs against other metal containing LDHs under acidic conditions [42]. Solution pH is playing a complex role in the sorption on to LDHs for all pollutants, however many different LDHs perform well at neutral pH, relating back to the pH-stability of the LDHs.

### 5.2. Role of temperature

Temperature impacts sorption processes due to the influence on mobility and solubility of the pollutant. Investigations of thermodynamic behaviour are also used in sorption studies to help aid an understanding of the sorption mechanism, through Gibbs free energy $\Delta G^\circ$, entropy $\Delta S^\circ$ and enthalpy $\Delta H^\circ$. Most sorption studies with LDH show to be a spontaneous endothermic process, with a positive $\Delta S^\circ$ and $\Delta H^\circ$ values observed. Many studies report that an increase in temperature results in an increased sorption capacity and removal efficiency, although these increases are not always significant. In the sorption of MO onto NiFe-LDHs the sorption capacity increases by around 10 mg/g over a temperature increase of 30 °C [43], and the removal efficiency of both CR and MO onto MgFe-LDH increased by 3% and 5% respectively again with a 30 °C increase [53]. A more comprehensive study was carried out looking at the sorption capacity of oxytetracycline onto CuMnAl-LDH at different temperatures (from 30 to 50 °C) for different initial concentrations of oxytetracycline, and an increase in sorption capacity was seen for all initial concentrations on sorbate at the highest temperatures, with maximum sorption capacity of 250.07 mg/g reported at 50 °C [78].

However there are some exceptions to these findings, such as the sorption of MO onto CoCu-LDH was found to be exothermic in nature with the sorption capacity of MO decreasing from 998 mg/g to 827 mg/g with an increase in temperature from 25 to 40 °C [52]. This behaviour was explained through the increase in randomness of the dye making sorption more difficult. Similar findings were reported for the sorption of norfloxacin onto MgAl-LDH, with the sorption capacity decreasing with an increase in temperature for varying initial concentration of the antibiotic, again reporting that the exothermic nature of the process may be due to the higher degree of mobility of sorbate at higher temperature [77].

It would be expected that adsorption mainly characterised by physisorption processes would be exothermic processes, however there are some chemisorption processes which may be expected to display an endothermic behaviour [88]. This of course becomes even more complex when multiple sorption mechanisms, including anion exchange, are likely to occur, with similar findings being highlighted in other reviews [29].

The impact on sorption as a result of temperature does not seem to be pollutant specific, with different relationships observed within studies of the same pollutants, and in most cases the impact of changing temperature is only minimal. However, it is important to consider if the optimum temperatures investigated would be representative of the temperatures of environmental wastewater effluent which would be treated by such sorbent materials.

### 5.3. Role of initial concentration of pollutant

Finding the most effective ratio of sorbent to sorbate is key in designing and operating an adsorption remediation technique in an economical way. In many sorption studies the initial concentrations of the pollutants used are usually at the mg/L range, whilst may be representative of dyes concentrations in the environment which have been reported to be up to 100's mg/L [89], it is unlikely to be the case for pharmaceuticals which are often reported to be found in concentrations down to ng/L in aqueous environments [74]. The initial pollutant concentrations used in some of the studies are up to 1700 mg/L [68], much higher than nearly all concentrations reported in the environment, hence could be skewing the assumptions regarding potential performance of the LDHs in the environment, especially as many studies found that the amount of pollutant adsorbed onto an LDH increased with increasing initial concentration of the pollutant. This increase at higher concentrations is likely to due to the diving force concentration gradient which overcome the mass transfer resistance, and this seen for different pollutants, both MO [40,48] and pharmaceuticals [78]. Other studies which have reported similar findings have also indicated this is due to adsorption being in monolayer at low initial MO concentration which then transition to a multilayer sorption as the initial concentration increases [50]. However, such findings are not universal, with Zaghouane-Boudiaf et al. [54] reporting that the removal percentage of MO decreased when the concentration of MO increased. This is explained through the finite number of adsorption sites on the LDH available, which corresponds to the decreasing percentage removal of the MO at higher initial concentrations.

In addition, changing initial concentration of the pollutant 2,4-D was found to result in different sorption mechanisms, seen through differing XRD patterns of the LDH following sorption. At the lowest concentrations of 2,4-D (below 0.4 mmol/L) there is no change in the XRD pattern of the LDH compared to the pre-sorption XRD pattern, indicating no change in the interlayer spacing or associated anion exchange. However at higher concentrations of 2,4-D (above 0.6 mol/L) changes in the XRD associated with the expansion of the interlayer space are observed indicating that anion exchange may be taking place [90]. This is not something which is widely considered in many studies, so should be something which more attention should be paid to understand if different sorption mechanisms dominate depending on the initial pollutant concentration and the role this may play in eventual sorption capacity or performance over fluctuating pollutant concentrations.

### *5.4. Contact time*

The kinetics of a sorption process are key to aid the understanding of how a sorption process can be scaled up. Primarily pseudo-first order and pseudo-second order kinetic models are used to investigate the process, and as can be seen across the examples presented the pseudo-second order model fits the sorption process. Although mass transfer and bulk transfer stages of the sorption process may also be playing a role, which may also impact the kinetics of the process [114,115].

Generally, it is found that adsorption onto an LDH is rapid over the initial time period, followed by a period of slower uptake before reaching a plateau at equilibrium. This is attributed to the greater number of adsorption sites accessible and available initially available, paired with the higher concentration of pollutant [40]. Various time frames are observed in the literature, with studies showing rapid sorption between 20 and 30 min, progressing to the plateau after around 90–120 min [40,53]. Although longer time frames, taking up to 8 h to reach equilibrium [91], and shorter time frames, reaching 100% removal after 30 min, are also observed [46,47]. Moving away from MO, pharmaceuticals pollutants have also observed similar findings, with the removal of metronidazole onto a MgAl-LDH, reaching equilibrium after around 100 min [75].

### *5.5. Presence of competing ions and real wastewater matrices*

Whilst many studies focus on the removal of single pollutants from aqueous solutions, in real wastewater matrices many different compounds will be present, resulting in either a mutually enhancing (synergetic) or inhibiting (antagonistic effect) the sorption of the targeted pollutant [92]. A decrease in removal efficiency was observed for MO sorption on LDHs because of presence of completing ions. The scale of the impact of each individual ion was put own to charge density and ionic radii, which effects their ability to enter the interlayer region of the LDH, with divalent and trivalent anions such as $SO_4^{2-}$ and $CO_3^{2-}$ having a greater impact on the removal efficiency, decreasing from 95% down to between 60% and 40%. $PO_4^{3-}$ is reported to have a different mechanism of disruption in which the metal cations in the LDH can be dissolved leading to a decrease in the adsorption capacity, rather than through competition for the adsorption sites [46]. This is in line with the effects of competing ions on the sorption of MO on to CoAl-LDHs [41]. Similarly, pharmaceutical sorption studies have also observed a decrease in removal efficiency with the presence of competing anions. However, a variation in the relationship was seen for carbonate ions in solutions, with the removal efficiency of metronidazole onto MgAl-LDH decreasing at low concentrations of carbonate, but the removal efficiency increased with increasing carbonate concentration which was attributed to the pH buffering effect of carbonate in solution [75].

Further studies have also observed decrease in removal efficiency through the presence of competing anions in the water matrix, and interestingly it was also found that the impact differed depending on the metals present in the LDH [76]. This is not something which is routinely considered in sorption studies, but of course will have a great impact on the applicability of the materials in environmental applications. More work is needed to understand how the anions disrupt the sorption, and how this could impact sorption capacity in real world situations.

Studies have also investigated co-adsorption, through the effect of metal ions in solution (Cu(II) and Cr (VI)) on oxytetracycline sorption on to CuMnAl-LDH. In this study the presence of both metals resulted in a decrease of adsorption capacity of oxytetracycline, with an increased impact at higher metal concentrations [78]. Such an effect may have a greater influence depending on the composition of the wastewater effluent to be treated by the sorbent material.

The removal of pollutants from environmental wastewater matrices has been highlighted in a limited number of studies. One such example is the use of the various LDHs as sorbent materials from an industrial dying factory, with the focus of this study on the removal of colour and decrease in chemical oxygen demand (COD) of the sample, with findings showing that 90% of the colour was removed through the use of ZnAl-Cl-LDH [93], However, in this study very limited data is presented about the specific characteristics of the waste water or how these may fluctuate over time, nor how the matrix of other chemicals present in the sample are impacting the behaviour of the LDH. Further work is needed to investigate how the performance of LDHs as sorbents is impacted by use in environmental wastewater systems moving on from synthetic waste waters, and this has been highlighted in other reviews which have considered LDH based materials on the removal of varying pollutants [94].

## 6. Considerations for technology transfer of LDHs

Further to the optimisation of operating conditions of an LDH based sorption solution for water remediation there are a range of other considerations for scaling up such a technology for pilot or even commercial applications. The reusability of such sorbent materials has a significant impact on their overall economic considerations and environmental impact [37]. There are two main pathways for the regeneration of LDHs, either through a thermal process or chemical approach leading to desorption of the pollutant. Thermal treatment approaches rely on the memory effect of LDHs, and include the calcination of the LDH materials to the mixed metal oxides before a subsequent exposure to aqueous environments containing the pollutant; whereas chemical options include washing the LDH with various solvents allowing for removal of the pollutant from the LDH, with examples of both seen in the literature (Table 2). As can be seen in Table 2, most of the studies are only looking at up to 5–6 regeneration cycles, however one study looked at up to 12 cycles, with the removal efficiency dropping off after the 7th cycle [95], highlighting the need for studies to consider greater numbers of cycles to explore the long-term possibilities for reuse of LDH sorbents. It is of course worth bearing in mind that this is not just an issue with LDHs, and is also an issue for other high-value sorbent materials [96]. Additionally the properties impacting the reusability of LDH has not been widely investigated, however it has been suggested that the metals present in the LDH may play a role in the sorption/desorption cycles through variation in pore structures, however this is not something which has been extensively explored in the literature [32].

For large-scale commercial usage of LDHs as sorbent materials a transition from batch sorption to alternative continuous sorption processes is required. Different approaches are reported in the literature, such as LDHs being used in dispersed powder form and in granular form in a fixed-bed [24]. Examples of LDH being tethered to solid supports can also be found. MgAl-LDH nanosheets and directionally arranged $\gamma$-AlO(OH) nanowires on to the surface of amorphous carbon have been utilised for minocycline removal [97]. There have also been reports of improved removal capacities, such as for the sorption of doxycycline using MgAl-LDH multiwalled carbon nanotubes against sorption onto free MgAl-LDH [79]. An alternative approach to commercial application of LDHs as sorbent materials is through the use of fixed-bed reactors [98]. MgAl-LDH and ZnAl-LDH have been used in fixed bed reactors for the sorption of the protein bovine serum albumin, which showed promising findings for the sorption and subsequent elution/regeneration of the LDH [99]. Fixed-bed column experiments also been used for the sorption of two pharmaceuticals by a ZnTiAl-LDH, however in this

**Table 2**
Summary of regeneration and reuse cycles of LDH sorbent materials.

| LDH | Sorbate | Regeneration technique | Number of cycles considered | Main findings | Reference |
|---|---|---|---|---|---|
| CoCu-LDH nanosheets | Methyl Orange | – | 5 | Removal percentage decreased from 99.7% down to 79.5% over fiver cycles. | [52] |
| FeMg-LDH | Congo Red; | Memory effect | 6 | Removal efficiency decreased from 98% to 86% | [53] |
| FeMg-LDH | Methyl Orange | Memory effect | 6 | Removal efficiency decreased from 90% to 80% | [53] |
| NiAl-LDH | Methyl Orange | Washing with distilled water | 5 | Removal efficiency decreased from 95% to 70% | [42] |
| NiAl-LDH | o-nitrophenol | Memory effect Calcination at 250 °C for 1 h | 5 | Sorption capacity decreased from approx. 125–65 mg/g – with the top sorption capacity maintained over 4 cycles | [76] |
| CaAl-LDH | o-nitrophenol | Memory effect Calcination at 250 °C for 1 h | 5 | Sorption capacity decreased from approx. 130–40 mg/g. Decrease in sorption capacity seen after the first reuse cycle | [76] |
| ZnAl-LDH | o-nitrophenol | Memory effect Calcination at 250 °C for 1 h | 5 | Sorption capacity decreased from approx. 130–30 mg/g. Decrease in sorption capacity seen after the first reuse cycle | [76] |
| NiCo-LDH | Congo Red | Washing with 15% dilute ammonia solution | 5 | Removal efficiency decreased from 99.5% to 73.2% | [81] |
| NiCo-LDH | Congo Red | Washed with ethanol at 80 °C | 5 | Removal efficiency stable across five cycles, from 100% to around 93.2% | [82] |
| NiCo-LDH | Rhodamine B | Washed with ethanol at 80 °C | 5 | Removal efficiency stable across five cycles, small decrease from around 80–70.6% | [82] |
| MgAl-His-LDH | Congo Red | Washed with mixture of ethanol and $NaNO_3$ until colourless | 12 | Removal efficiency achieved above $\geq$ 95% in first 7 cycles, then slowly decreasing with increasing cycles | [95] |
| MgAl-His-LDH | Indigo Carmine | Washed with mixture of ethanol and $NaNO_3$ until colourless | 12 | Removal efficiency achieved above $\geq$ 95% in first 7 cycles, then slowly decreasing with increasing cycles | [95] |
| MgAl-His-LDH | Sunset Yellow | Washed with mixture of ethanol and $NaNO_3$ until colourless | 12 | Removal efficiency achieved above $\geq$ 95% in first 7 cycles, then slowly decreasing with increasing cycles | [95] |

research the LDH was calcined prior to application as a sorbent [100]. There are limited examples of studies in literature of LDHs being used in their uncalcined state as sorbent materials in fixed bed reactors and there is a clear opportunity for more research in this area due to the established nature of fixed-bed reactors.

Finally, to be able to utilise LDH materials on a large scale there is a need to be able to manufacture them on a commercial scale. Whilst batch coprecipitation is the most common preparation technique for LDHs there are drawbacks including difficulties in controlling particle size and distribution of the LDHs, and inherent issues with scaling up a batch process. Various solutions have been cited including a technique utilising separate nucleation and aging steps [101], a novel in-line dispersion-precipitation method [102] and utilising a continuous flow hydrothermal method [22]. The final technique has been shown to be scalable, producing up to 10's of kg per hour of LDH material, with the LDHs displaying similar properties to the particles produced in bench scale reactors [103]. Few of these approaches have been used to synthesis LDHs then utilised as sorbent materials for ECs, which is an area of research which requires further development.

To understand if adsorption technologies would be suitable for commercial use each of the factors impacting potential commercial use of such materials need to be considered from a holistic point of view. This can be carried out through metrics such as a life cycle assessment (LCA) or technoeconomic analysis, which considers the manufacture, application, and regeneration of the LDH sorbent. To date, very few LCA or techno-economic analysis have been conducted on any aspects of LDH, particular in relation to the pharmaceutical industry and/or municipal waste waters which contain pharmaceutical pollutants. There are limited studies which have focused directly on LCA on such aspects of other materials such as synthesis of metal oxides [104] or comparison of sustainability of adsorption and ion exchange technologies for Arsenic removal [105]. Furthermore, recent LCAs explore the efficiency of adsorbents on pharmaceuticals wastes, such as granular activated carbon [106], wood biomass and charcoal [107], and hydrochar adsorbents [108].

The scope of any LCA analysis on LDH adsorbents need to consider the LDH manufacture and pollutant adsorption phases to ensure that whole life cycle impacts are considered. When combined with Life Cycle Costing (LCC) this allows the optimal business proposition to be identified. Corominas et al. [109] recently proposed guidelines for LCAs for wastewater treatment systems to enable comparison between systems and technologies. A further consideration for LDHs' is the difference in bench scale produced and applied LDHs and full scale LDHs and application, which has shown not to be comparable in terms of operational parameters [103]. Future studies should include techno-economic and environmental analysis to gain a fuller appreciation of the viability and efficiency of LDH adsorbents for pharmaceutical remediation.

## 7. Summary and future recommendations

The diversity of different studies reported demonstrates the clear potential for LDHs to be applied as a simple, cost effective sorbent materials for removing ECs and other organic pollutants from water streams. However, further research is required to understand which LDH properties are most important for sorption applications to allow for more tailored design of the most effective LDHs for the sorption of organic pollutants. This improved understanding would allow researchers to truly utilise the tuneable nature of LDHs arising from the range of metal cations and anions which can be combined and the host of different preparation techniques available. There are a range of properties of the LDH which play a role in the performance of individual LDHs as sorbent materials including the ratios of the divalent and trivalent metals and the nature of the initial interlayer anions, and this holds true over a range of different organic pollutants. The textual properties of the LDHs also impact the sorption performance of LDHs. Whilst the specific surface area of the LDH particles is often reported, other properties such as morphology of the particles and associated pore structure are not often discussed, and if these were to be reported more it would aid advancing the understanding of this complex structure-activity relationship. Further to this, the synthesis method used in the preparation of the LDH also play a role, especially in the light of potential carbonate contamination known to block anion exchange - and for a similar reason a detailed characterisation of the nature of the interlayer anion should be provided to allow for an understanding of which sorption mechanisms may be taking place, which in turn can impact the preferred divalent to trivalent metal ratio.

For the purpose of comparing findings across different pollutants it is important to consider that whilst there are general similarities in the findings and trends, the characteristics of the pollutant does play a role in the sorption capacity of the LDH. There is a lot of scope for further work in this area to be able to design more targeted high-performing sorbent materials. In the first instance more comparative studies should be reported, concentrating on the impact of single variables on the physiochemical properties of the LDHs and subsequent sorption capacity. Additionally, novel LDHs, including those which display 3D morphologies should be considered for the removal of ECs, such as pharmaceuticals, over the more traditional dye studies. Further to this, for any future commercial application of such a technology issues such as reuse cycles, application in dynamic and continuous fixed bed systems and the LDH performance under realistic environmental pollutant conditions should be considered more widely in future studies. Such studies should also include a consideration of the performance of the LDH sorbent materials on waste waters taken from the environment, as well as on spiked or synthetic water. As highlighted, there are also a lack of studies considering the full life cycle assessment, technoeconomic or cost analysis of such processes, and such studies would add valuable insights into the viability of LDHs as sorbent materials.

## 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

The authors would also like to acknowledge the Engineering and Physical Sciences Research Council for funding of the EPSRC Centre for Doctoral Training in Sustainable Chemistry (Grant number EP/L015633/1).

## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2021.105197.

## References

[1] United Nations, 2019. Special Edition: Progress towards the Sustainable Development Goals Report of the Secretary-General, E/2019/68.

[2] United Nations World Water Assessment Programme, 2017. The United Nations World Water Development Report 2017: Wastewater, The Untapped Resource. UNESCO, Paris.

[3] T. Rasheed, M. Bilal, F. Nabeel, M. Adeel, H.M.N. Iqbal, Environmentally-related contaminants of high concern: potential sources and analytical modalities for detection, quantification, and treatment, Environ. Int. 122 (2019) 52–66, https://doi.org/10.1016/j.envint.2018.11.038.

[4] L.K.M. Chow, T.M. Ghaly, M.R. Gillings, A survey of sub-inhibitory concentrations of antibiotics in the environment, J. Environ. Sci. 99 (2021) 21–27, https://doi.org/10.1016/j.jes.2020.05.030.

[5] M.B. Ahmed, J.L. Zhou, H.H. Ngo, W. Guo, N.S. Thomaidis, J. Xu, Progress in the biological and chemical treatment technologies for emerging contaminant removal from wastewater: a critical review, J. Hazard. Mater. 323 (2017) 274–298, https://doi.org/10.1016/j.jhazmat.2016.04.045.

[6] D.P. Mohapatra, D.M. Kirpalani, Advancement in treatment of wastewater: fate of emerging contaminants, Can. J. Chem. Eng. 97 (2019) 2621–2631, https://doi.org/10.1002/cjce.23533.

[7] J.C. Muñoz-Senmache, S. Kim, R.R. Arrieta-Pérez, C.M. Park, Y. Yoon, A. J. Hernández-Maldonado, Activated carbon–metal organic framework composite for the adsorption of contaminants of emerging concern from water, ACS Appl. Nano Mater. 3 (2020) 2928–2940, https://doi.org/10.1021/acsanm.0c00190.

[8] UK Water Industry Research, 2019. The Big Questions Facing the Water Industry.

[9] T. Rasheed, M. Bilal, A.A. Hassan, F. Nabeel, R.N. Bharagava, L.F. Romanholo Ferreira, H.N. Tran, H.M.N. Iqbal, Environmental threatening concern and efficient removal of pharmaceutically active compounds using metal-organic frameworks as adsorbents, Environ. Res. 185 (2020), 109436, https://doi.org/10.1016/j.envres.2020.109436.

[10] J.R. de Andrade, M.F. Oliveira, M.G.C. da Silva, M.G.A. Vieira, Adsorption of pharmaceuticals from water and wastewater using nonconventional low-cost materials: a review, Ind. Eng. Chem. Res. 57 (2018) 3103–3127, https://doi.org/10.1021/acs.iecr.7b05137.

[11] L.S. Rocha, D. Pereira, É. Sousa, M. Otero, V.I. Esteves, V. Calisto, Recent advances on the development and application of magnetic activated carbon and char for the removal of pharmaceutical compounds from waters: a review, Sci. Total Environ. 718 (2020), 137272, https://doi.org/10.1016/j.scitotenv.2020.137272.

[12] H. Zhang, S. Pap, M.A. Taggart, K.G. Boyd, N.A. James, S.W. Gibb, A review of the potential utilisation of plastic waste as adsorbent for removal of hazardous priority contaminants from aqueous environments, Environ. Pollut. 258 (2020), 113698, https://doi.org/10.1016/j.envpol.2019.113698.

[13] A. Carmalin Sophia, E.C. Lima, N. Allaudeen, S. Rajan, Application of graphene based materials for adsorption of pharmaceutical traces from water and wastewater- a review, Desalin. Water Treat. 57 (2016) 27573–27586, https://doi.org/10.1080/19443994.2016.1172989.

[14] Q. Liu, Yi Zhou, J. Lu, Yanbo Zhou, Novel cyclodextrin-based adsorbents for removing pollutants from wastewater: a critical review, Chemosphere 241 (2020), 125043, https://doi.org/10.1016/j.chemosphere.2019.125043.

[15] W. Feitknecht, M. Gerber, Zur kenntnis der doppelhydroxyde und basischen doppelsalze III. Über Magnesium-Aluminiumdoppelhydroxyd, Helv. Chim. Acta 25 (1942) 131–137, https://doi.org/10.1002/hlca.19420250115.

[16] F. Cavani, F. Trifirò, A. Vaccari, Hydrotalcite-type anionic clays: preparation, properties and applications, Catal. Today 11 (1991) 173–301, https://doi.org/10.1016/0920-5861(91)80068-K.

[17] G. Mishra, B. Dash, S. Pandey, Layered double hydroxides: a brief review from fundamentals to application as evolving biomaterials, Appl. Clay Sci. 153 (2018) 172–186, https://doi.org/10.1016/j.clay.2017.12.021.

[18] J. He, M. Wei, B. Li, Y. Kang, D.G. Evans, Xue Duan, Preparation of layered double hydroxides, in: X. Duan, D.G. Evans (Eds.), Layered Double Hydroxides, Springer, Berlin, Heidelberg, 2006, pp. 89–119, https://doi.org/10.1007/430_006.

[19] S. Mallakpour, M. Hatami, C.M. Hussain, Recent innovations in functionalized layered double hydroxides: fabrication, characterization, and industrial applications, Adv. Colloid Interface Sci. 283 (2020), 102216, https://doi.org/10.1016/j.cis.2020.102216.

[20] M.V. Bukhtiyarova, A review on effect of synthesis conditions on the formation of layered double hydroxides, J. Solid State Chem. 269 (2019) 494–506, https://doi.org/10.1016/j.jssc.2018.10.018.

[21] N. Chubar, R. Gilmour, V. Gerda, M. Mičušík, M. Omastova, K. Heister, P. Man, J. Fraissard, V. Zaitsev, Layered double hydroxides as the next generation inorganic anion exchangers: synthetic methods versus applicability, Adv. Colloid Interface Sci. 245 (2017) 62–80, https://doi.org/10.1016/j.cis.2017.04.013.

[22] Q. Wang, S.V.Y. Tang, E. Lester, D. O'Hare, Synthesis of ultrafine layered double hydroxide (LDHs) nanoplates using a continuous-flow hydrothermal reactor, Nanoscale 5 (2013) 114–117, https://doi.org/10.1039/C2NR32568C.

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

[24] K.-H. Goh, T.-T. Lim, Z. Dong, Application of layered double hydroxides for removal of oxyanions: a review, Water Res. 42 (2008) 1343–1368, https://doi.org/10.1016/j.watres.2007.10.043.

[25] F. Ogata, N. Nagai, M. Kishida, T. Nakamura, N. Kawasaki, Interaction between phosphate ions and Fe-Mg type hydrotalcite for purification of wastewater, J. Environ. Chem. Eng. 7 (2019), 102897, https://doi.org/10.1016/j.jece.2019.102897.

[26] X. Liang, Y. Zang, Y. Xu, X. Tan, W. Hou, L. Wang, Y. Sun, Sorption of metal cations on layered double hydroxides, Colloids Surf. A Physicochem. Eng. Asp. 433 (2013) 122–131, https://doi.org/10.1016/j.colsurfa.2013.05.006.

[27] P. Gu, S. Zhang, X. Li, Xiangxue Wang, T. Wen, R. Jehan, A. Alsaedi, T. Hayat, Xiangke Wang, Recent advances in layered double hydroxide-based nanomaterials for the removal of radionuclides from aqueous solution, Environ. Pollut. 240 (2018) 493–505, https://doi.org/10.1016/j.envpol.2018.04.136.

[28] P. Li, P. Chen, Z. Liu, S. Nie, X. Wang, G. Wang, W. Zhang, H. Chen, L. Wang, Highly efficient elimination of uranium from wastewater with facilely synthesized Mg-Fe layered double hydroxides: optimum preparation conditions and adsorption kinetics, Ann. Nucl. Energy 140 (2020), 107140, https://doi.org/10.1016/j.anucene.2019.107140.

[29] Z. Yang, F. Wang, C. Zhang, G. Zeng, X. Tan, Z. Yu, Y. Zhong, H. Wang, F. Cui, Utilization of LDH-based materials as potential adsorbents and photocatalysts for the decontamination of dyes wastewater: a review, RSC Adv. 6 (2016) 79415–79436, https://doi.org/10.1039/C6RA12727D.

[30] M. Daud, A. Hai, F. Banat, M.B. Wazir, M. Habib, G. Bharath, M.A. Al-Harthi, A review on the recent advances, challenges and future aspect of layered double hydroxides (LDH) – containing hybrids as promising adsorbents for dyes removal, J. Mol. Liq. 288 (2019), 110989, https://doi.org/10.1016/j.molliq.2019.110989.

[31] D. Chaara, I. Pavlovic, F. Bruna, M.A. Ulibarri, K. Draoui, C. Barriga, Removal of nitrophenol pesticides from aqueous solutions by layered double hydroxides and their calcined products, Appl. Clay Sci. 50 (2010) 292–298, https://doi.org/10.1016/j.clay.2010.08.002.

[32] N. Hashim, S.N.M. Sharif, M.Z. Hussein, I.M. Isa, A. Kamari, A. Mohamed, N. M. Ali, S.A. Bakar, M. Mamat, Layered hydroxide anion exchanger and their applications related to pesticides: a brief review, Mater. Res. Innov. 21 (2017) 129–145, https://doi.org/10.1080/14328917.2016.1192717.

[33] J.S. Calisto, I.S. Pacheco, L.L. Freitas, L.K. Santana, W.S. Fagundes, F.A. Amaral, S.C. Canobre, Adsorption kinetic and thermodynamic studies of the 2, 4 – dichlorophenoxyacetate (2,4-D) by the [Co–Al–Cl] layered double hydroxide, Heliyon 5 (2019), e02553, https://doi.org/10.1016/j.heliyon.2019.e02553.

[34] E. Li, L. Liao, G. Lv, Z. Li, C. Yang, Y. Lu, The interactions between three typical PPCPs and LDH, Front. Chem. 6 (2018) 1–9, https://doi.org/10.3389/fchem.2018.00016.

[35] M. Chen, P. Wu, Z. Huang, J. Liu, Y. Li, N. Zhu, Z. Dang, Y. Bi, Environmental application of MgMn-layered double oxide for simultaneous efficient removal of tetracycline and Cd pollution: performance and mechanism, J. Environ. Manag. 246 (2019) 164–173, https://doi.org/10.1016/j.jenvman.2019.06.002.

[36] M. Rosset, L.W. Sfreddo, G.E.N. Hidalgo, O.W. Perez-Lopez, L.A. Féris, Adsorbents derived from hydrotalcites for the removal of diclofenac in wastewater, Appl. Clay Sci. 175 (2019) 150–158, https://doi.org/10.1016/j.clay.2019.04.014.

[37] M. Zubair, M. Daud, G. McKay, F. Shehzad, M.A. Al-Harthi, Recent progress in layered double hydroxides (LDH)-containing hybrids as adsorbents for water remediation, Appl. Clay Sci. 143 (2017) 279–292, https://doi.org/10.1016/j.clay.2017.04.002.

[38] A. Li, H. Deng, C. Ye, Y. Jiang, Fabrication and characterization of novel ZnAl-layered double hydroxide for the superadsorption of organic contaminants from wastewater, ACS Omega 5 (2020) 15152–15161, https://doi.org/10.1021/acsomega.0c01092.

[39] A. Mittal, A. Malviya, D. Kaur, J. Mittal, L. Kurup, Studies on the adsorption kinetics and isotherms for the removal and recovery of Methyl Orange from wastewaters using waste materials, J. Hazard. Mater. 148 (2007) 229–240, https://doi.org/10.1016/j.jhazmat.2007.02.028.

[40] L. Ai, C. Zhang, L. Meng, Adsorption of Methyl Orange from aqueous solution on hydrothermal synthesized Mg–Al layered houble hydroxide, J. Chem. Eng. Data 56 (2011) 4217–4225, https://doi.org/10.1021/je200743u.

[41] Y. Chen, C. Jing, X. Zhang, D. Jiang, X. Liu, B. Dong, L. Feng, S. Li, Y. Zhang, Acid-salt treated CoAl layered double hydroxide nanosheets with enhanced adsorption capacity of Methyl Orange dye, J. Colloid Interface Sci. 548 (2019) 100–109, https://doi.org/10.1016/j.jcis.2019.03.107.

[42] K. El Hassani, B.H. Beakou, D. Kalnina, E. Oukani, A. Anouar, Effect of morphological properties of layered double hydroxides on adsorption of azo dye Methyl Orange: a comparative study, Appl. Clay Sci. 140 (2017) 124–131, https://doi.org/10.1016/j.clay.2017.02.010.

[43] J. Gao, Y. Lu, L. Fang, F. Wu, F. Ling, T. Guan, L. Shi, B. Hu, F. Meng, Efficient removal of Methyl Orange and heavy metal ion from aqueous solution by NiFe-Cl-layered double hydroxide, Environ. Eng. Sci. 35 (2017) 373–381, https://doi.org/10.1089/ees.2017.0023.

[44] T. Guan, L. Fang, Y. Lu, F. Wu, F. Ling, J. Gao, B. Hu, F. Meng, X. Jin, A facile approach to synthesize 3D flower-like hierarchical NiCo layered double hydroxide microspheres and their enhanced adsorption capability, Colloids Surf. A Physicochem. Eng. Asp. 529 (2017) 907–915, https://doi.org/10.1016/j.colsurfa.2017.06.049.

[45] Z. Jiang, L. Yan, J. Wu, X. Liu, J. Zhang, Y. Zheng, Y. Pei, Low-temperature synthesis of carbonate-intercalated NixFe-layered double hydroxides for enhanced adsorption properties, Appl. Surf. Sci. 531 (2020), 147281, https://doi.org/10.1016/j.apsusc.2020.147281.

[46] C. Jing, Y. Chen, Xing Zhang, X. Guo, X. Liu, B. Dong, F. Dong, Xianming Zhang, Y. Liu, S. Li, Y. Zhang, Low carbonate contaminative and ultrasmall NiAl LDH prepared by acid salt treatment with high adsorption capacity of Methyl Orange, Ind. Eng. Chem. Res. 58 (2019) 11985–11998, https://doi.org/10.1021/acs.iecr.9b01706.

[47] N. Li, Z. Chang, H. Dang, Y. Zhan, J. Lou, S. Wang, S. Attique, W. Li, H. Zhou, C. Sun, Deep eutectic solvents assisted synthesis of MgAl layered double hydroxide with enhanced adsorption toward anionic dyes, Colloids Surf. A: Physicochem. Eng. Asp. 591 (2020), 124507, https://doi.org/10.1016/j.colsurfa.2020.124507.

[48] Y. Lin, Z. Zeng, J. Zhu, Y. Wei, S. Chen, X. Yuan, L. Liu, Facile synthesis of ZnAl-layered double hydroxide microspheres with core–shell structure and their enhanced adsorption capability, Mater. Lett. 156 (2015) 169–172, https://doi.org/10.1016/j.matlet.2015.04.032.

[49] F. Ling, L. Fang, Y. Lu, J. Gao, F. Wu, M. Zhou, B. Hu, A novel CoFe layered double hydroxides adsorbent: high adsorption amount for Methyl Orange dye and fast removal of Cr(VI), Microporous Mesoporous Mater. 234 (2016) 230–238, https://doi.org/10.1016/j.micromeso.2016.07.015.

[50] Y. Lu, B. Jiang, L. Fang, F. Ling, J. Gao, F. Wu, X. Zhang, High performance NiFe layered double hydroxide for Methyl Orange dye and Cr(VI) adsorption, Chemosphere 152 (2016) 415–422, https://doi.org/10.1016/j.chemosphere.2016.03.015.

[51] K. Morimoto, K. Tamura, N. Iyi, J. Ye, H. Yamada, Adsorption and photodegradation properties of anionic dyes by layered double hydroxides, J. Phys. Chem. Solids 72 (2011) 1037–1045, https://doi.org/10.1016/j.jpcs.2011.05.018.

[52] S. Saghir, E. Fu, Z. Xiao, Synthesis of CoCu-LDH nanosheets derived from zeolitic imidazole framework-67 (ZIF-67) as an efficient adsorbent for azo dye from waste water, Microporous Mesoporous Mater. 297 (2020), 110010, https://doi.org/10.1016/j.micromeso.2020.110010.

[53] R. Shabbir, A. Gu, J. Chen, M.M. Khan, P. Wang, Y. Jiao, Z. Zhang, Y. Liu, Y. Yang, Highly efficient removal of congo red and Methyl Orange by using petal-like Fe-Mg layered double hydroxide, Int. J. Environ. Anal. Chem. (2020) 1–18, https://doi.org/10.1080/03067319.2020.1730343.

[54] H. Zaghouane-Boudiaf, M. Boutahala, L. Arab, Removal of Methyl Orange from aqueous solution by uncalcined and calcined MgNiAl layered double hydroxides (LDHs), Chem. Eng. J. 187 (2012) 142–149, https://doi.org/10.1016/j.cej.2012.01.112.

[55] Y.-M. Zheng, N. Li, W.-D. Zhang, Preparation of nanostructured microspheres of Zn–Mg–Al layered double hydroxides with high adsorption property, Colloids Surf. A Physicochem. Eng. Asp. 415 (2012) 195–201, https://doi.org/10.1016/j.colsurfa.2012.10.014.

[56] I. Langmuir, The adsorption of gases on plane surfaces of glass, mic and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403, https://doi.org/10.1021/ja02242a004.

[57] Y.-S. Ho, Review of second-order models for adsorption systems, J. Hazard. Mater. 136 (2006) 681–689, https://doi.org/10.1016/j.jhazmat.2005.12.043.

[58] Y. Liu, Y.-J. Liu, Biosorption isotherms, kinetics and thermodynamics, Sep. Purif. Technol. 61 (2008) 229–242, https://doi.org/10.1016/j.seppur.2007.10.002.

[59] Y.-F. Chao, J.-J. Lee, S.-L. Wang, Preferential adsorption of 2,4-dichlorophenoxyacetate from associated binary-solute aqueous systems by Mg/Al-$NO_3$ layered double hydroxides with different nitrate orientations, J. Hazard. Mater. 165 (2009) 846–852, https://doi.org/10.1016/j.jhazmat.2008.10.063.

[60] E. Conterosito, L. Palin, D. Antonioli, D. Viterbo, E. Mugnaioli, U. Kolb, L. Perioli, M. Milanesio, V. Gianotti, Structural characterisation of complex layered double hydroxides and TGA-GC-MS study on thermal response and carbonate contamination in nitrate- and organic-exchanged hydrotalcites, Chem. – A Eur. J. 21 (2015) 14975–14986, https://doi.org/10.1002/chem.201500450.

[61] G. Carja, R. Nakamura, T. Aida, H. Niiyama, Textural properties of layered double hydroxides: effect of magnesium substitution by copper or iron, Microporous Mesoporous Mater. 47 (2001) 275–284, https://doi.org/10.1016/S1387-1811(01)00387-0.

[62] M.B. Ahmed, J.L. Zhou, H.H. Ngo, W. Guo, Adsorptive removal of antibiotics from water and wastewater: progress and challenges, Sci. Total Environ. 532 (2015) 112–126, https://doi.org/10.1016/j.scitotenv.2015.05.130.

[63] M. Thommes, Physical adsorption characterization of nanoporous materials, Chem. Ing. Tech. 82 (2010) 1059–1073, https://doi.org/10.1002/cite.201000064.

[64] C. Peng, J. Dai, J. Yu, J. Yin, Calcined Mg-Fe layered double hydroxide as an absorber for the removal of Methyl Orange, AIP Adv. 5 (2015), 057138, https://doi.org/10.1063/1.4921455.

[65] M. Laipan, J. Yu, R. Zhu, J. Zhu, A.T. Smith, H. He, D. O'Hare, L. Sun, Functionalized layered double hydroxides for innovative applications, Mater. Horiz. 7 (2020) 715–745, https://doi.org/10.1039/C9MH01494B.

[66] J. Akhtar, N.A.S. Amin, K. Shahzad, A review on removal of pharmaceuticals from water by adsorption, Desalin. Water Treat. 57 (2016) 12842–12860, https://doi.org/10.1080/19443994.2015.1051121.

[67] I. Clark, J. Smith, R. Gomes, E. Lester, Continuous synthesis of $Zn_2Al$-$CO_3$ layered double hydroxides for the adsorption of reactive dyes from water, J. Environ. Chem. Eng. 7 (2019), 103175, https://doi.org/10.1016/j.jece.2019.103175.

[68] G. Darmograi, B. Prelot, G. Layrac, D. Tichit, G. Martin-Gassin, F. Salles, J. Zajac, Study of adsorption and intercalation of orange-type dyes into Mg–Al layered double hydroxide, J. Phys. Chem. C 119 (2015) 23388–23397, https://doi.org/10.1021/acs.jpcc.5b05510.

[69] R. Shan, L. Yan, Y. Yang, K. Yang, S. Yu, H. Yu, B. Zhu, B. Du, Highly efficient removal of three red dyes by adsorption onto Mg–Al-layered double hydroxide, J. Ind. Eng. Chem. 21 (2015) 561–568, https://doi.org/10.1016/j.jiec.2014.03.019.

[70] Z. Cai, A.D. Dwivedi, W.-N. Lee, X. Zhao, W. Liu, M. Sillanpää, D. Zhao, C.-H. Huang, J. Fu, Application of nanotechnologies for removing pharmaceutically active compounds from water: development and future trends, Environ. Sci. Nano 5 (2018) 27–47, https://doi.org/10.1039/C7EN00644F.

[71] Â. Almeida, M. Solé, A.M.V.M. Soares, R. Freitas, Anti-inflammatory drugs in the marine environment: bioconcentration, metabolism and sub-lethal effects in marine bivalves, Environ. Pollut. 263 (2020), 114442, https://doi.org/10.1016/j.envpol.2020.114442.

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

[73] E. Felis, J. Kalka, A. Sochacki, K. Kowalska, S. Bajkacz, M. Harnisz, E. Korzeniewska, Antimicrobial pharmaceuticals in the aquatic environment - occurrence and environmental implications, Eur. J. Pharmacol. 866 (2020), 172813, https://doi.org/10.1016/j.ejphar.2019.172813.

[74] S.R. Hughes, P. Kay, L.E. Brown, Global synthesis and critical evaluation of pharmaceutical data sets collected from river systems, Environ. Sci. Technol. 47 (2013) 661–677, https://doi.org/10.1021/es3030148.

[75] M.N. Sepehr, T.J. Al-Musawi, E. Ghahramani, H. Kazemian, M. Zarrabi, Adsorption performance of magnesium/aluminum layered double hydroxide nanoparticles for metronidazole from aqueous solution, Arab. J. Chem. 10 (2017) 611–623, https://doi.org/10.1016/j.arabjc.2016.07.003.

[76] B.S. Marques, K. Dalmagro, K.S. Moreira, M.L.S. Oliveira, S.L. Jahn, T.A. de Lima Burgo, G.L. Dotto, Ca–Al, Ni–Al and Zn–Al LDH powders as efficient materials to treat synthetic effluents containing o-nitrophenol, J. Alloy. Compd. 838 (2020), 155628, https://doi.org/10.1016/j.jallcom.2020.155628.

[77] M. Sui, Y. Zhou, L. Sheng, B. Duan, Adsorption of norfloxacin in aqueous solution by Mg–Al layered double hydroxides with variable metal composition and interlayer anions, Chem. Eng. J. 210 (2012) 451–460, https://doi.org/10.1016/j.cej.2012.09.026.

[78] J.O. Eniola, R. Kumar, A.A. Al-Rashdi, M.A. Barakat, Hydrothermal synthesis of structurally variable binary CuAl, MnAl and ternary CuMnAl hydroxides for oxytetracycline antibiotic adsorption, J. Environ. Chem. Eng. 8 (2020), 103535, https://doi.org/10.1016/j.jece.2019.103535.

[79] S.A.A. Moaty, R.K. Mahmoud, N.A. Mohamed, Y. Gaber, A.A. Farghali, M.S.M. A. Wahed, H.A. Younes, Synthesis and characterisation of LDH-type anionic nanomaterials for the effective removal of doxycycline from aqueous media, Water Environ. J. 34 (2019), https://doi.org/10.1111/wej.12526.

[80] Z.P. Xu, Y. Jin, S. Liu, Z.P. Hao, G.Q. Lu, Surface charging of layered double hydroxides during dynamic interactions of anions at the interfaces (Max),

J. Colloid Interface Sci. 326 (2008) 522–529, https://doi.org/10.1016/j.jcis.2008.06.062.

[81] H. Hu, J. Liu, Z. Xu, L. Zhang, B. Cheng, W. Ho, Hierarchical porous Ni/Co-LDH hollow dodecahedron with excellent adsorption property for congo red and Cr (VI) ions, Appl. Surf. Sci. 478 (2019) 981–990, https://doi.org/10.1016/j.apsusc.2019.02.008.

[82] X. Wang, W. Zhou, C. Wang, Z. Chen, Cotton fiber-supported layered double hydroxides for the highly efficient adsorption of anionic organic pollutants in water, New J. Chem. 42 (2018) 9463–9471, https://doi.org/10.1039/C8NJ00678D.

[83] R. Lafi, K. Charradi, M.A. Djebbi, A. Ben Haj Amara, A. Hafiane, Adsorption study of congo red dye from aqueous solution to Mg–Al–layered double hydroxide, Adv. Powder Technol. 27 (2016) 232–237, https://doi.org/10.1016/j.apt.2015.12.004.

[84] C. Zhang, S. Yang, H. Chen, H. He, C. Sun, Adsorption behavior and mechanism of reactive brilliant red X-3B in aqueous solution over three kinds of hydrotalcite-like LDHs, Appl. Surf. Sci. 301 (2014) 329–337, https://doi.org/10.1016/j.apsusc.2014.02.073.

[85] J. Matusik, Y. Deng, Fumonisin B1 interaction with Mg-Al and Mg-Fe layered double hydroxides: removal efficiency and mechanisms, Materials 13 (2020) 4344, https://doi.org/10.3390/ma13194344.

[86] S.-L. Wang, P.-C. Wang, In situ XRD and ATR-FTIR study on the molecular orientation of interlayer nitrate in Mg/Al-layered double hydroxides in water, Colloids Surf. A Physicochem. Eng. Asp. 292 (2007) 131–138, https://doi.org/10.1016/j.colsurfa.2006.06.014.

[87] F.P. de Sá, B.N. Cunha, L.M. Nunes, Effect of pH on the adsorption of sunset yellow FCF food dye into a layered double hydroxide (CaAl-LDH-NO3), Chem. Eng. J. 215–216 (2013) 122–127, https://doi.org/10.1016/j.cej.2012.11.024.

[88] J.M. Thomas, The existence of endothermic adsorption, J. Chem. Educ. 38 (1961) 138, https://doi.org/10.1021/ed038p138.

[89] D.A. Yaseen, M. Scholz, Textile dye wastewater characteristics and constituents of synthetic effluents: a critical review, Int. J. Environ. Sci. Technol. 16 (2019) 1193–1226, https://doi.org/10.1007/s13762-018-2130-z.

[90] A. Legrouri, M. Lakraimi, A. Barroug, A. De Roy, J.P. Besse, Removal of the herbicide 2,4-dichlorophenoxyacetate from water to zinc–aluminium–chloride layered double hydroxides, Water Res. 39 (2005) 3441–3448, https://doi.org/10.1016/j.watres.2005.03.036.

[91] Z. Li, B. Yang, S. Zhang, B. Wang, B. Xue, A novel approach to hierarchical sphere-like ZnAl-layered double hydroxides and their enhanced adsorption capability, J. Mater. Chem. A 2 (2014) 10202–10210, https://doi.org/10.1039/C4TA01028K.

[92] M. Turabik, Adsorption of basic dyes from single and binary component systems onto bentonite: simultaneous analysis of Basic Red 46 and Basic Yellow 28 by first order derivative spectrophotometric analysis method, J. Hazard. Mater. 158 (2008) 52–64, https://doi.org/10.1016/j.jhazmat.2008.01.033.

[93] F.Z. Mahjoubi, A. Khalidi, O. Cherkaoui, R. Elmoubarki, M. Abdennouri, N. Barka, Treatment of textile effluents by chloride-intercalated Zn-, Mg- and Ni-Al layered double hydroxides, J. Water Reuse Desalin. 7 (2016) 307–318, https://doi.org/10.2166/wrd.2016.041.

[94] M. Zubair, I. Ihsanullah, H. Abdul Aziz, M. Azmier Ahmad, M.A. Al-Harthi, Sustainable wastewater treatment by biochar/layered double hydroxide composites: progress, challenges, and outlook, Bioresour. Technol. 319 (2021), 124128, https://doi.org/10.1016/j.biortech.2020.124128.

[95] M. Shamsayei, Y. Yamini, H. Asiabi, Fabrication of zwitterionic histidine/layered double hydroxide hybrid nanosheets for highly efficient and fast removal of anionic dyes, J. Colloid Interface Sci. 529 (2018) 255–264, https://doi.org/10.1016/j.jcis.2018.06.022.

[96] L. Wang, C. Shi, L. Wang, L. Pan, X. Zhang, J.-J. Zou, Rational design, synthesis, adsorption principles and applications of metal oxide adsorbents: a review, Nanoscale 12 (2020) 4790–4815, https://doi.org/10.1039/C9NR09274A.

[97] J. Li, N. Zhang, D.H.L. Ng, Synthesis of a 3D hierarchical structure of γ-AlO(OH)/Mg–Al-LDH/C and its performance in organic dyes and antibiotics adsorption, J. Mater. Chem. A 3 (2015) 21106–21115, https://doi.org/10.1039/C5TA04497A.

[98] E.J. Henley, Separation process principles, in: Ernest J. Henley, J.D. Seader, D. Keith Roper (Eds.), Separation Process Principles, 3rd ed., John Wiley & Sons, Hoboken, 2011.

[99] K.A.B. Nogueira, J.A. Cecilia, S.O. Santos, J.E. Aguiar, E. Vilarrasa-García, E. Rodríguez-Castellón, D.C.S. Azevedo, I.J. Silva, Adsorption behavior of bovine serum albumin on Zn–Al and Mg–Al layered double hydroxides, J. Sol-Gel Sci. Technol. 80 (2016) 748–758, https://doi.org/10.1007/s10971-016-4166-1.

[100] L. Santamaría, M. López-Aizpún, M. García-Padial, M.A. Vicente, S.A. Korili, A. Gil, Zn-Ti-Al layered double hydroxides synthesized from aluminum saline slag wastes as efficient drug adsorbents, Appl. Clay Sci. 187 (2020), 105486, https://doi.org/10.1016/j.clay.2020.105486.

[101] Y. Zhao, F. Li, R. Zhang, D.G. Evans, X. Duan, Preparation of layered double-hydroxide nanomaterials with a uniform crystallite size using a new method involving separate nucleation and aging steps, Chem. Mater. 14 (2002) 4286–4291, https://doi.org/10.1021/cm020370h.

[102] S. Abelló, J. Pérez-Ramírez, Tuning nanomaterials' characteristics by a miniaturized in-line dispersion–precipitation method: application to hydrotalcite synthesis, Adv. Mater. 18 (2006) 2436–2439, https://doi.org/10.1002/adma.200600673.

[103] I. Clark, R.L. Gomes, C. Crawshaw, L. Neve, R. Lodge, M. Fay, C. Winkler, M. Hull, E. Lester, Continuous synthesis of $Zn_2Al–CO_3$ layered double hydroxides: a comparison of bench, pilot and industrial scale syntheses, React. Chem. Eng. 4 (2019) 663–666, https://doi.org/10.1039/C8RE00241J.

[104] P. Caramazana-González, P.W. Dunne, M. Gimeno-Fabra, M. Zilka, M. Ticha, B. Stieberova, F. Freiberg, J. McKechnie, E.H. Lester, Assessing the life cycle environmental impacts of titania nanoparticle production by continuous flow solvo/hydrothermal syntheses, Green Chem. 19 (2017) 1536–1547, https://doi.org/10.1039/C6GC03357A.

[105] A. Dominguez-Ramos, K. Chavan, V. García, G. Jimeno, J. Albo, K.V. Marathe, G. D. Yadav, A. Irabien, Arsenic removal from natural waters by adsorption or ion exchange: an environmental sustainability assessment, Ind. Eng. Chem. Res. 53 (2014) 18920–18927, https://doi.org/10.1021/ie4044345.

[106] Y. Li, S. Zhang, W. Zhang, W. Xiong, Q. Ye, X. Hou, C. Wang, P. Wang, Life cycle assessment of advanced wastewater treatment processes: involving 126 pharmaceuticals and personal care products in life cycle inventory, J. Environ. Manag. 238 (2019) 442–450, https://doi.org/10.1016/j.jenvman.2019.01.118.

[107] I. Kozyatnyk, D.M.M. Yacout, J. Van Caneghem, S. Jansson, Comparative environmental assessment of end-of-life carbonaceous water treatment adsorbents, Bioresour. Technol. 302 (2020), 122866, https://doi.org/10.1016/j.biortech.2020.122866.

[108] S. Román, J.M. Valente Nabais, B. Ledesma, C. Laginhas, M.-M. Titirici, Surface interactions during the removal of emerging contaminants by hydrochar-based adsorbents, Molecules 25 (2020) 2264, https://doi.org/10.3390/molecules25092264.

[109] L. Corominas, D.M. Byrne, J.S. Guest, A. Hospido, P. Roux, A. Shaw, M.D. Short, The application of life cycle assessment (LCA) to wastewater treatment: a best practice guide and critical review, Water Res. 184 (2020), 116058, https://doi.org/10.1016/j.watres.2020.116058.

[114] M. Hubbe, S. Azizian, S. Douven, Implications of Apparent Pseudo-Second-Order Adsorption Kinetics onto Cellulosic Materials: A Review, BioResources 14 (2019) 7582–8626.

[115] H. Tran, S. You, A. Hosseini-Bandegharaei, H. Chao, Mistakes and inconsistencies regarding adsorption of contaminants from aqueous solutions: A critical review, Water Res. 120 (2017) 88–116, https://doi.org/10.1016/j.watres.2017.04.014.

## Further reading

[1] H.A. Younes, R. Khaled, H.M. Mahmoud, H.F. Nassar, M.M. Abdelrahman, F.I. Abo El-Ela, M. Taha, Computational and experimental studies on the efficient removal of diclofenac from water using ZnFe-layered double hydroxide as an environmentally benign absorbent, J. Taiwan Inst. Chem. Eng. 102 (2019) 297–311, https://doi.org/10.1016/j.jtice.2019.06.018.

[2] A. Zaher, M. Taha, A.A. Farghali, R.K. Mahmoud, 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 (2020) 12256–12269, https://doi.org/10.1007/s11356-020-07750-3.

[3] K. Nejati, S. Davary, M. Saati, Study of 2,4-dichlorophenoxyacetic acid (2,4-D) removal by Cu-Fe-layered double hydroxide from aqueous solution, Appl. Surf. Sci. 280 (2013) 67–73, https://doi.org/10.1016/j.apsusc.2013.04.086.

[4] Q. Wang, X. Wang, C. Shi, LDH nanoflower lantern derived from ZIF-67 and its application for adsorptive removal of organics from water, Ind. Eng. Chem. Res. 57 (2018) 12478–12484, https://doi.org/10.1021/acs.iecr.8b01324.