



A review of the removal of anions and oxyanions of the halogen elements from aqueous solution by layered double hydroxides



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ABSTRACT

The application of layered double hydroxides (LDHs) and thermally activated LDHs for the removal of various fluorine (F^- , BF_4^-), chlorine (Cl^- , ClO_4^-), bromine (Br^- , BrO_3^-) and iodine (I^- , IO_3^-) species from aqueous solutions has been reviewed in this article. LDHs and thermally activated LDHs were able to significantly reduce the concentration of selected anions in laboratory scale experiments. The $M^{2+}:M^{3+}$ cation ratio of the LDH adsorbent was an important factor which influenced anion uptake. Though LDHs were able to remove some target anion species through anion exchange and surface adsorption thermal activation and reformation generally produced better results. The presence of competing anions including carbonate, phosphate and sulphate had a significant impact on uptake of the target anion as LDHs typically exhibit lower affinity towards monovalent anions compared to anions with multiple charges. The removal of fluoride and perchlorate from aqueous solution by a continuous flow system utilising fixed bed columns packed with LDH adsorbents has also been investigated. The adsorption capacity of the columns at breakpoint was heavily dependent on the flow rate and lower than result reported for the corresponding batch methods. There is still considerable scope for future research on numerous topics summarised in this article.

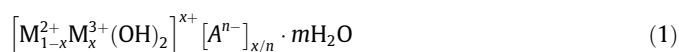
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1. Introduction

Providing the world's growing population with safe drinking water for will undoubtedly prove to be a major challenge in the coming century. Access to clean and reliable sources of potable water is vital for good health, however, many natural and anthropogenic sources can contaminate water sources making them unsafe [1]. Some anions and oxyanions of the halogen elements (fluorine, chlorine, bromine, and iodine) are of particular concern because of their toxic [2–5], mutagenic [4], carcinogenic [4] and radioactive [1,6,7] properties. These include not just the halide ions but also several oxyanions which are described in greater detail in their relevant sections below.

Layered double hydroxides (LDHs) are an interesting group of clay minerals which have been applied to the removal of numerous anionic pollutants from aqueous solution. Also known as anionic clays or hydrotalcite like materials LDHs consist of a layered structure similar to that of the mineral brucite ($Mg(OH)_2$). In LDHs a number of the divalent cations (M^{2+}) if the brucite structure are substituted with a trivalent cation (M^{3+}) resulting in a layered structure which carries a net positive charge that is balanced by

exchangeable anions intercalated into the interlayer regions [8–10]. LDHs can be represented by the general formula:



where M^{2+} is the divalent cation, M^{3+} is the trivalent cation, A^{n-} is the exchangeable anion (usually carbonate, chloride or nitrate) and $0.2 < x < 0.33$ [8–10].

In addition to their natural anion exchange property (which is unique among the clay minerals) LDHs also exhibit the reformation (or memory) effect, another important and useful property. Thermal activation of a LDH, which is usually achieved by calcination in air at 300–500 °C causes the elimination of interlayer water and anions resulting in the formation of a mixed metal oxide (or thermally activated LDH) in which the divalent and trivalent metal oxides are dispersed at the molecular level rather than the particle level [11,12]. If a thermally activated LDH is exposed to water and charge balancing anions spontaneous reformation of a LDH structure may occur. The reformed LDH may not be identical to that of the original structure as it may contain different anions intercalated into the interlayer region [8,13,14]. The reformation effect has been successfully utilised to improve the anion uptake capacity of LDHs. Thermal activation temperature is an important factor that usually plays a significant impact on anion uptake. The optimum thermal activation temperature is the temperature at which the maximum number of interlayer anions is removed without

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causing a permanent decomposition of the LDH cation layers. Excessive heating of a LDH result in its decomposition to oxides which cannot exhibit reformation or anion exchange properties. The optimum thermal activation temperature determined experimentally is usually below 500 °C [8,13,14].

The adsorption of anions by LDHs and thermally activated LDHs is usually investigated by fitting experimental results to some common surface adsorption isotherm models including the Langmuir and Freundlich isotherms. The Langmuir adsorption isotherm is one of the simplest models used to describe adsorption onto the surface of a solid. The Langmuir model is based on three significant assumptions [15]:

- (1) The maximum possible adsorption corresponds to complete monolayer coverage of the adsorbent (i.e. multilayer adsorption is not possible).
- (2) All surface sites on the adsorbent are uniform (of the same binding energy).
- (3) Adsorption sites are independent of each other. The vacancy or occupation of any particular site does not affect neighbouring sites.

The Langmuir isotherm is described by the Langmuir equation:

$$q_e = \frac{QbC_e}{1 + bC_e} \quad (2)$$

where q_e is the adsorption loading, Q and b are Langmuir constants and C_e is the equilibrium concentration.

The Freundlich adsorption isotherm is a model that can be used to describe more complex adsorption behaviour. The Freundlich isotherm attempts to overcome some of the deficiencies in the Langmuir model by modelling the effect of a heterogeneous surface [15].

The Freundlich isotherm is described by the Freundlich equation:

$$q_e = k_f C_e^n \quad (3)$$

where q_e is the adsorption loading, k_f and n are Freundlich constants and C_e is the equilibrium concentration.

The Langmuir–Freundlich adsorption isotherm is a combination of the Langmuir and Freundlich isotherms that have not been widely applied to the sorption of anionic species by LDHs and thermally activated LDHs. The Langmuir–Freundlich isotherm is described by the following equation [16,17].

$$q_e = \frac{KC_e^{1/n}}{1 + bC_e^{1/n}} \quad (4)$$

where q_e is the adsorption loading, K , b and n are constants and C_e is the equilibrium concentration. The cost of adsorbents and catalysts is an important factor which may contribute to the widespread uptake of new processes by industry. Consequently adsorbents which can be obtained at low cost or even produced from waste products have been of considerable interest in recent years [18–24]. LDHs exist in minable deposits and are already prepared synthetically at an industrial scale, making them promising candidates for industrial applications.

In this article, the authors aim to summarise the removal of selected anions (including: F^- , BF_4^- , Cl^- , ClO_4^- , Br^- , BrO_3^- , and IO_3^-) from aqueous solution by LDHs and thermally activated LDHs by anion exchange, reformation and redox mechanisms.

2. Removal of fluorine species from aqueous solution by LDHs

2.1. Sources and toxicity of fluoride (F^-): introduction

Fluoride is an essential element required in small amounts for optimal health. Fluoride is found in many foodstuffs and is often deliberately added to drinking water, table salt and dental care products to protect against tooth decay. Water sources in some parts of the world exceed the World Health Organisation's (WHO) Guideline value of 1.5 mg/L due to natural or anthropogenic sources. Long term exposure to water containing high levels of fluoride may lead to dental and skeletal fluorosis. Dental fluorosis, can occur at fluoride concentrations between 0.9 and 1.2 mg/L while skeletal fluorosis, a potentially serious and crippling medical condition usually occurs at fluoride concentrations of 3–10 mg/L. Fluoride in groundwater may be due to the presence of naturally occurring fluoride minerals such as fluorspar (CaF_2), cryolite ($Na_3(AlF_6)$) and fluorapatite ($Ca_5(PO_4)_3F$) [1]. In addition to natural sources, numerous industrial processes including aluminium refining and the burning of some coals can also release fluoride into the environment. The methods currently available for the removal of fluoride from drinking water are complex and costly. Because of their anion exchange and reformation properties LDHs may be able to provide a simpler and more economical method for the removal of fluoride from drinking water and other aqueous solutions. A number of key publications reported in the literature concerning the removal of fluoride from aqueous solution using LDHs and thermally activated LDHs have been summarised in this section.

2.2. Removal of fluoride (F^-) from aqueous solution by Mg/Al LDHs

Wang et al. [25] investigated the removal of fluoride by 3:1 Mg/Al LDHs and thermally activated LDHs. LDHs were prepared by conventional co-precipitation followed by hydrothermal ageing for 24 h. LDHs were thermally activated by calcination at 500 °C in air over 3 h [25]. Fluoride sorption was carried out using sodium fluoride solutions prepared by serial dilution of a 1000 mg/L stock solution. Fluoride concentrations were determined using a fluoride ion selective electrode [25]. The 3:1 LDH without any thermal activation exhibited a low fluoride uptake of only 29.8%. The maximum fluoride uptake achieved without thermal activation was 33.8% and was with achieved with an initial fluoride concentration of 3.31 mg/L [25]. Thermal activation resulted in a significant increase in fluoride uptake by LDHs. The thermally activated Mg/Al LDH was able to achieve a maximum fluoride removal of 75.8% under similar conditions [25]. Adsorption isotherms were plotted but could not be fitted to the Langmuir adsorption isotherm model. Wang et al. chose to fit the experimental results to a straight line with a gradient of 0.46 L/g [25]. Fluoride uptake was directly proportional to contact time during the first 15 min of the reaction, at which point the reaction reached equilibrium. Fluoride uptake remained relatively constant after 15 min [25].

Lv et al. [12] investigated the removal of fluoride from aqueous solution by thermally activated Mg/Al LDHs with varying Mg:Al cation ratios (2:1, 3:1 and 4:1) [12]. The LDHs were prepared by urea method followed by calcination in a muffle furnace for 2 h at various temperatures ranging from 200 to 800 °C. Thermal activation temperature had a significant impact on fluoride uptake, with fluoride adsorption increasing with thermal activation temperature. The maximum fluoride uptake occurred at 500 °C with an adsorption capacity of 80 mg/g [12]. Lv et al. proposed that the optimum thermal activation temperature corresponded to the maximum removal of interlayer carbonate. Composition of the LDH cation layers also had a significant impact on fluoride uptake, with the thermally activated 2:1 Mg/Al LDH the most

effective fluoride adsorbent [12]. Lv et al. attributed the higher fluoride uptake of the 2:1 LDH to the greater specific surface area of the 2:1 LDH rather than its higher charge density (Table 1). The optimum LDH adsorbent dose was 2.0 g/1.8 L of and the optimum initial fluoride concentration was 200 mg/L [12]. Solution pH also had a significant impact on fluoride adsorption, with the maximum fluoride adsorption of 88.0% occurring at a pH 6.0. Lv et al. proposed that the slightly acidic conditions remove hydroxide ions (OH^-) which compete with fluoride for binding sights on the adsorbent. Under more acidic conditions the thermally activated LDH adsorbent may begin to dissolve also causing a reduction of the fluoride uptake capacity [12,26].

Fluoride adsorption isotherms were plotted and compared to the Langmuir and Freundlich adsorption isotherm models (Fig. 1). The Freundlich isotherm gave a better fit to the experimental results ($R^2 = 0.9908$) indicating that fluoride sorption by Mg/Al LDHs may have been a multilayer or heterogenous process [12]. Lv et al. also concluded that the kinetics of fluoride sorption was best described by the second-order kinetic model [12]. Finally, Lv et al. investigated the effect of competing anions including phosphate (PO_4^{3-}), Sulphate (SO_4^{2-}), chloride (Cl^-), Bromide (Br^-) and nitrate (NO_3^-) on fluoride sorption. While nitrate had no significant impact on fluoride uptake, the other anions caused fluoride sorption to decrease. Phosphate ions had the greatest impact on fluoride uptake followed by chloride, sulphate, bromide and nitrate. Lv et al. concluded that anions with higher charge density had a greater effect on fluoride uptake by Mg/Al LDH adsorbents [12].

2.3. Removal of fluoride (F^-) from aqueous solution by Zn/Al LDHs

Lv et al. [12] compared the fluoride uptake capacity of Mg/Al and Zn/Al LDHs. Lv et al. (Fig. 2). determined that the fluoride uptake capacity of Zn/Al LDHs was lower than those of the Mg/Al LDHs, and attributed this effect to the higher atomic weight of zinc which lowered the overall anion exchange capacity per gram of the LDH [12].

Das et al. [27] investigated the removal of fluoride by thermally activated Zn/Al LDHs. A 2:1 Zn/Al LDH was prepared by co-precipitation at constant pH, with portions of the LDHs thermally activated by calcination at 450 °C over 8 h [27] (Fig. 3). Fluoride sorption increased with contact time reaching equilibrium after 4 h with 85.5% fluoride removal. Fluoride uptake did not continue to increase significantly after 4 h contact time [27]. Initial solution pH was a variable which had a significant impact on fluoride uptake. Maximum uptake occurred at pH 6.0, which was the same optimum pH reported by Lv et al. for Mg/Al LDHs [12]. The optimum initial fluoride concentration for the Zn/Al LDHs was 60 mg/L. Fluoride sorption also decreased with reaction temperature, suggesting that the fluoride adsorption process was exothermic in nature [27].

Fluoride sorption data were plotted and compared to the Langmuir adsorption isotherm model (Fig. 4). It is important to note

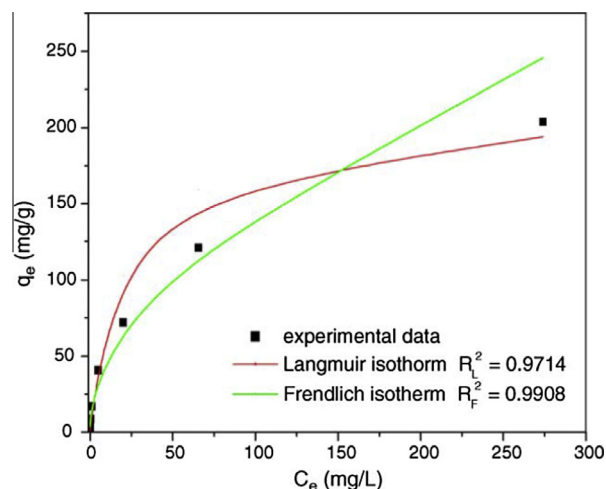


Fig. 1. Langmuir and Freundlich adsorption isotherms for the removal of fluoride by thermally activated Mg/Al LDHs at 30 °C prepared by Lv et al. Figure reprinted with permission from [12].

that other groups have found that the Freundlich isotherm (which was not used in this article) better described the sorption of fluoride by other LDHs [27]. Das et al. calculated several significant thermodynamic parameters including the standard Gibbs free energy (ΔG^0 , -25.61 kJ/mol), standard enthalpy of change (ΔH^0 , -5.66 kJ/mol) and standard entropy of change (ΔS^0 , 63.75 J/mol/K). The negative ΔG^0 and ΔH^0 values confirmed the spontaneous and exothermic nature of fluoride sorption [27]. Finally Das et al. investigated the effect of phosphate and sulphate on the sorption of fluoride by Zn/Al LDHs. Fluoride uptake decreased to 24.34% when the initial concentration of phosphate reached 10 mg/L. Sulphate ions had a less significant effect on fluoride sorption which only decreased to 15.44% when the initial sulphate concentration reached 30 mg/L.

2.4. Removal of fluoride (F^-) from aqueous solution by Mg/Al, Ni/Al and Co/Al LDHs

Jiménez-Núñez et al. [16] compared the application of thermally activated Mg/Al, Ni/Al and Co/Al LDHs for the removal of fluoride from aqueous solution. Thermally activated LDHs were prepared by conventional co-precipitation followed by calcination at approximately 842 °C (723 K) for 3 h [16]. Jiménez-Núñez et al. determined the thermally activated Mg/Al LDH had the highest fluoride uptake capacity of 0.46 mg/g under equilibrium conditions. The uptake capacity of thermally activated Ni/Al LDH was only slightly lower at 0.45 mg/g and thermally activated Co/Al LDH exhibited the lowest uptake capacity of 0.39 mg/g [16].

Fluoride adsorption isotherms were plotted and fitted to the Langmuir, Freundlich and Langmuir–Freundlich adsorption isotherm models. The Langmuir–Freundlich isotherm model was the best fit for the experimental data and Jiménez-Núñez et al. concluded that the main mechanism of fluoride uptake was chemisorption by a heterogeneous LDH adsorbent [16]. Jiménez-Núñez et al. [17] also investigated the possibility of using Ni/Al for fluoride removal in a continuous flow system utilising packed columns with a diameter of 8 mm and a height of 14 or 28 mm. The fixed bed columns were packed with Ni/Al LDH adsorbent (0.5 and 1.0 g). Fluoride solutions (with concentrations of 5 and 6.85 mg/L) were introduced to the columns with a flow rate of 2 mL/min [17]. The fluoride adsorption capacity up to breakpoint of the continuous system (3.65 mg/g) was lower than that of the batch system (5.35 mg/g). Jiménez-Núñez et al. proposed that decrease in

Table 1

The effect of calcination temperature and surface area on fluoride sorption reported by Lv et al. Data from [12].

| Mg/Al ratio | Calcination temperature (°C) | Surface area (m^2/g) | Fluoride removal (%) |
|-------------|------------------------------|--|----------------------|
| 2:1 | 200 | 76.8 | 69.88 |
| 2:1 | 400 | 122.2 | 77.89 |
| 2:1 | 500 | 240.6 | 85.53 |
| 2:1 | 600 | 213.6 | 66.55 |
| 2:1 | 800 | 39.9 | 53.24 |
| 3:1 | 500 | 223.3 | 73.43 |
| 4:1 | 500 | 208.5 | 72.29 |

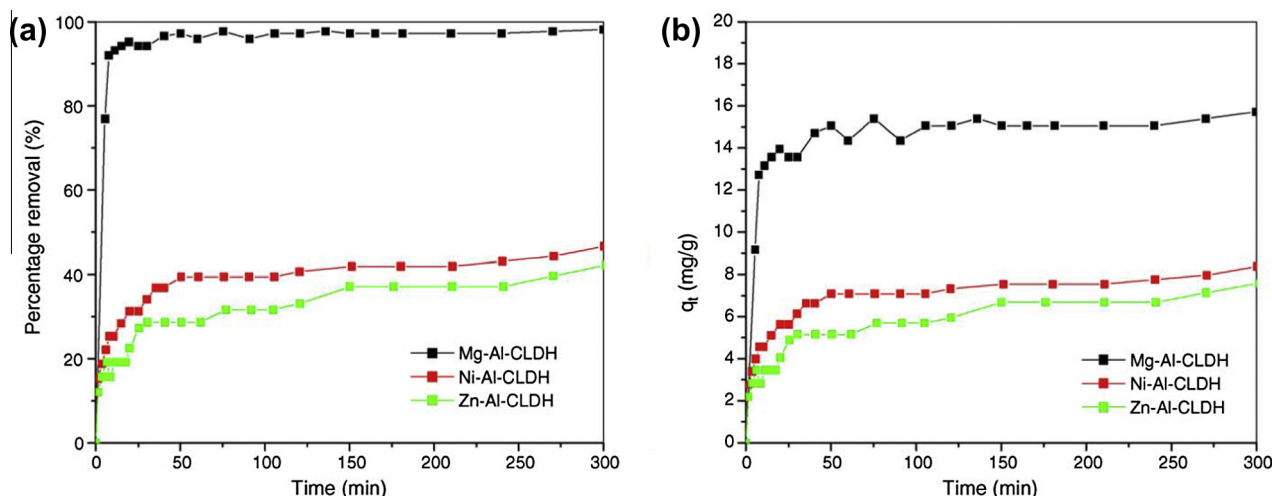


Fig. 2. comparison of the (a) percentage fluoride removal and (b) fluoride adsorption loading of thermally activated Mg/Al, Ni/Al and Zn/Al LDHs reported by Lv et al. (experimental conditions: 30 °C, initial fluoride solution 1.8L of 20 mg/L, adsorbent dose 2.0 g, pH 6.0). Figure reprinted with permission from [12].

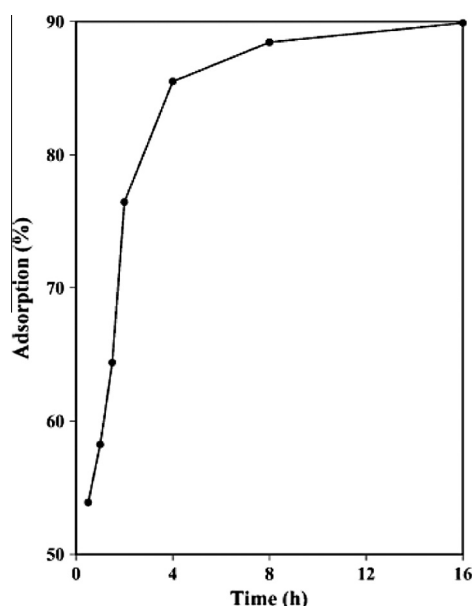


Fig. 3. Effect of contact time on fluoride adsorption capacity of Zn/Al LDHs reported by Das et al. Figure reprinted with permission from [27].

the flow rate would likely improve the fluoride sorption capacity [17].

2.5. Removal of fluoride (F^-) from aqueous solution by Li/Al LDHs

Zhang et al. [28] prepared Li/Al LDHs and used these materials for the removal of fluoride from aqueous solution. The 2:1 Li/Al LDHs were prepared by two different methods: co-precipitation and the urea method. The initial solution pH had a significant impact on fluoride sorption with the greater uptake occurring under slightly acidic conditions. The co-precipitated LDH consistently exhibited higher fluoride uptake than the LDH synthesised by urea hydrolysis. The optimal dose of the co-precipitated LDH was 1.0 g (the volume of solution used in the experiment was not reported) [28]. Adsorption isotherms were plotted and fitted to the Langmuir and Freundlich models. The Freundlich isotherm gave a better fit to the experimental data indicating that fluoride adsorption by the Li/Al LDH was a heterogeneous or multilayer process. Zhang et al.

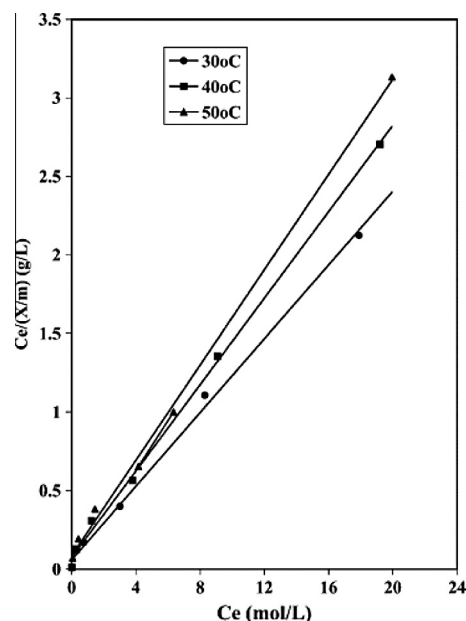


Fig. 4. Langmuir adsorption isotherm plots of fluoride adsorption by Zn/Al LDHs at different temperatures. Figure reprinted with permission from Das et al. [27].

concluded that this may have been due to the heterogeneous structure of the LDH surface [28]. The kinetics of fluoride uptake was investigated using several models including the pseudo-first-order, pseudo-second-order and inter-particle diffusion models. Zhang et al. determined that the pseudo-second-order model best described the experimental results ($R^2 > 0.99$). The rate limiting step of the fluoride sorption mechanism was described as a surface reaction, possibly chemisorption of fluoride onto the LDH [28].

2.6. Removal of tetrafluoroborate (BF_4^-) from synthetic wastewater by Mg/Al LDHs

The tetrafluoroborate (BF_4^-) ion may be formed in wastewaters containing both fluoride and boric acid in a certain pH range. Yoshioka et al. [29] investigated the potential of a thermally activated Mg/Al LDH as an adsorbent for the removal of tetrafluoroborate from a simulated wastewater solution. The simulated wastewater solution was prepared by allowing a 1 mM solution

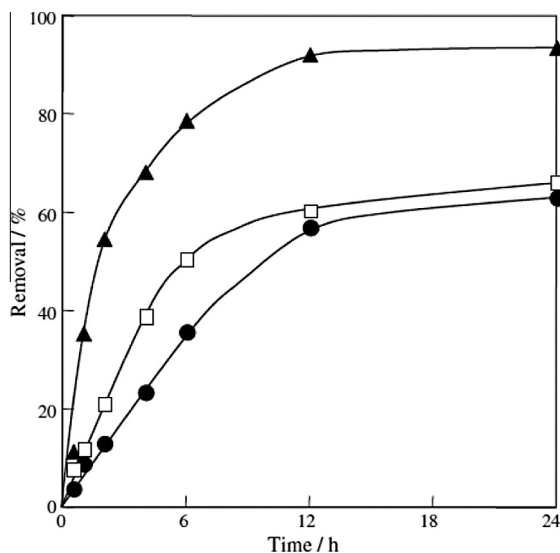


Fig. 5. Effect of contact time on the removal of BF_4^- (●), F^- (▲) and boron (□) from aqueous solution by thermally activated Mg/Al LDH. Figure reprinted with permission from Yoshioka et al. [29].

of NaBF_4 to stand for approximately one month. When analysed the simulated wastewater solution contained: tetrafluoroborate (0.47 mM), fluoride (F^- , 2.10 mM) and boric acid (H_3BO_3 , 0.53 M) [29]. A 4:1 Mg/Al LDH adsorbent was prepared by the co-precipitation method (described in [30]), followed by thermal activated at 500 °C for approximately 1 h [29]. Tetrafluoroborate uptake was measured by ion chromatography and determined from the residual concentration remaining after treatment with the thermally activated LDH adsorbent.

A 93% removal of tetrafluoroborate occurred after 24 h indicating that thermally activated 4:1 Mg/Al LDHs adsorbents may be suitable for the treatment of wastewaters contaminated with tetrafluoroborate (Fig. 5) [29]. Yoshioka et al. reported a decrease in the Mg:Al ratio (from 4:1 to 3.6:1 suggesting that partial dissolution of the LDH adsorbent may have occurred during contact with the tetrafluoroborate solution [29]. As tetrafluoroborate is reported to be thermodynamically unstable in the pH range of 10–11 used during the adsorption experiments, it is still currently unclear whether the tetrafluoroborate anion was removed from solution or if it was decomposed into fluoride and boric acid, which were then taken up by the adsorbent [29]. Yoshioka et al. proposed that the equilibration time of the tetrafluoroborate hydrolysis reaction may be in excess of 24 h, however, the slightly faster rate of fluoride removal (compared to boron removal) does not support this conclusion, indicating that at least partial hydrolysis did indeed occur [29].

The LDH adsorbent recovered after reformation in the simulated tetrafluoroborate wastewater was not thoroughly investigated by Yoshioka et al. It is therefore impossible to determine the composition of the interlayer region of the LDH. The LDH may have indeed contained tetrafluoroborate anions or simply a mixture of fluoride and borates. Further characterisation of the LDH residues may help elucidate the mechanism of tetrafluoroborate sorption by thermally activated LDHs. Powerful techniques including powder XRD, FTIR and ^{11}B MAS nuclear magnetic resonance spectroscopy (NMR) may provide valuable insights into the mechanism of tetrafluoroborate uptake.

2.7. Removal of fluorine species from aqueous solutions by LDHs: conclusions and recommendations for future work

There have been numerous significant publications on the removal of fluoride from aqueous solution by LDHs and thermally

activated LDHs. The structure of the LDH adsorbent appeared to have had a significant impact on fluoride sorption. The optimal $\text{M}^{2+}:\text{M}^{3+}$ ratio of 2:1 was attributed to the charge density of the adsorbent as well as differences in the surface properties of the materials. Mg/Al and Ni/Al LDHs exhibited higher fluoride uptake than the corresponding Zn/Al and Co/Al LDHs, however, no sufficient explanation for this effect has been provided. No articles concerning the substitution of the trivalent metal cation on fluoride sorption have appeared in the recent literature.

Thermal activation improved fluoride sorption with optimal fluoride uptake occurred under slightly acidic conditions (typically pH 6.0). At this pH, there are fewer hydroxide ions (OH^-) to compete with fluoride for binding sites and the LDH adsorbent does not dissolve.

Fluoride sorption also appeared to be both spontaneous and exothermic in nature and was better described by the Freundlich adsorption isotherm model than the Langmuir model, suggesting that fluoride sorption was a multilayer or heterogeneous surface process. The presence of anions with high charge density (particularly phosphate) significantly reduced fluoride uptake. Anions with lower charge density (such as nitrate) had a significantly smaller impact fluoride uptake.

3. Removal of chlorine species from aqueous solution by LDHs

3.1. Sources and toxicity of chloride (Cl^-) and perchlorate (ClO_4^-): introduction

Chloride in water is not regarded generally as a significant problem. The recommended dietary intake of chloride is 9 mg/kg of body mass [31]. The health effects of chloride appear to depend on nature of the cation (particularly sodium) rather than the chloride anion itself. Chloride toxicity has been observed in some rare cases, particularly in individuals with impaired sodium chloride metabolism. In one particular case, a sodium chloride dose of 1 g/kg of body mass was reported to be lethal in the case of a 9 week old child [1,31]. The perchlorate anion (ClO_4^-) is a powerful oxidising agent that can be released into the environment from a number of industrial sources [3]. Perchlorate is known to inhibit the transport of iodine to the thyroid gland, thus impairing its ability to synthesis key thyroid hormones [3,32]. There is also some evidence to suggest that perchlorate exposure may increase the risk of neurodevelopmental impairment in both foetuses and young children, leading the U.S. Environmental Protection Agency (EPA) to propose that perchlorate in drinking water should be regulated [3,32].

3.2. Removal of chloride (Cl^-) from aqueous solution by LDHs

Lv et al. [33] investigated the removal of chloride from aqueous solution using Zn/Al LDHs by an anion exchange mechanism. 2:1, 3:1 and 4:1 Zn/Al LDHs with interlayer nitrate were prepared by conventional co-precipitation and characterised by powder XRD, Fourier transform infrared spectroscopy (FTIR) and elemental analysis by inductively coupled plasma optical emission spectroscopy (ICP-OES) [33]. The Zn:Al ratio of the adsorbent had a significant effect on chloride sorption, which decreased with increase in Zn:Al molar ratio. The 2:1 Zn/Al LDH exhibited the highest anion exchange capacity of 64.14 mg/g followed by the 3:1 LDH (41.00 mg/g) and the 4:1 LDH (21.08 mg/g). All further experiments were carried out with the 2:1 Zn/Al LDH as it gave the best result [33]. Initial solution pH appeared to have little effect on chloride sorption with a maximum chloride uptake capacity of 19.84 mg/g achieved at pH 7.0. Lv et al. concluded that at low pH partial dissolution of the LDH occurred causing a reduction of

chloride uptake. At high pH the additional hydroxide ions present compete with chloride for binding sites in the LDH interlayer [33]. Percentage chloride removal increased with adsorbent dose, however, chloride uptake capacity decreased with increase in adsorbent dose. The optimal adsorption time was 4 h [33].

Equilibrium isotherms were plotted and compared to both the Langmuir and Freundlich adsorption isotherm models (Fig. 6). The Langmuir gave a better fit to the experimental data and was used to determine thermodynamic parameters at 40 °C including: Gibbs free energy (ΔG^0 , -14.79 kJ/mol), standard enthalpy of change (ΔH^0 , 5.89 kJ/mol) and standard entropy of change (ΔS^0 , 65.70 J/mol/K) [33]. These results indicate that the chloride adsorption process was a spontaneous and entropy driven process that was endothermic in nature [33]. The kinetics of chloride sorption was best described by pseudo-second order kinetic model [33].

3.3. Removal of perchlorate (ClO_4^-) from aqueous solution by LDHs

Wu et al. [3] investigated the removal of perchlorate by thermally activated Zn/Al LDHs prepared by a co-precipitation method involving separate nucleation and ageing processes [3,26]. LDHs were thermally activated by calcination in a muffle furnace for 3 h at 500 °C. The thermally activated LDH with a Zn:Al ratio of 2:1 was found to have the highest perchlorate sorption capacity of 99.85 mg/g. This effect was attributed to the higher charge density of this LDH [3]. The optimum dose of thermally activated Zn/Al LDH was 1.0 g/L resulting in 93.9% perchlorate removal. Increasing the adsorbent dose beyond 1.0 g/L did not have a significant effect on anion uptake. Doubling the adsorbent dose to 2.0 g/L only increased perchlorate uptake to 96.7% [3].

Equilibrium isotherms for perchlorate sorption were plotted and compared to the Langmuir and Freundlich adsorption isotherm models. The Freundlich isotherm provided the best fit for the experimental data suggesting that perchlorate sorption was a multilayer process [3]. The Gibbs free energy (ΔG^0) of perchlorate uptake was calculated as -1.4 kJ/mol. The negative value of the Gibbs free energy confirmed the spontaneous nature of the adsorption process [3]. The kinetics of perchlorate uptake by the LDH was best described by a modified multiplex model, indicating perchlorate sorption mechanism involved a combination of first and second order kinetics. Wu et al. concluded that perchlorate sorption mechanism involved two processes. The first was a rapid diffusion controlled step, followed by a slower step controlled by the rate of the reaction between perchlorate and the thermally activated LDH [3].

Wu et al. investigated the effect of introducing competing anions including phosphate (PO_4^{3-}) and sulphate (SO_4^{2-}) on the uptake

of perchlorate by thermally activated LDHs. Perchlorate uptake decreased with increasing phosphate or sulphate concentration. Perchlorate removal was decreased to only 10% when the concentration of competing anions was over 100 mg/L. The overall order of anion affinity was: $\text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{ClO}_4^-$ [3]. Finally, Wu et al. also investigated the sorption of perchlorate by thermally activated LDHs using a continuous flow system [3]. Fixed bed columns were prepared with an internal diameter of 8 mm and a height of 85 mm. A flow rate of 5 mL/min resulted in an adsorption capacity up to breakpoint of 60.5 mg/g (Fig. 7). When the flow rate was decreased to 2 mL/min the adsorption capacity increased to 90.5 mg/g, which was close to the result obtained from the batch system [3].

3.4. Removal of chlorine species from aqueous solutions by LDHs: conclusions and recommendations for future work

LDHs with high charge density (divalent to trivalent ratio of 2:1) appeared to show the greatest affinity for anionic chlorine species. Mg/Al and Zn/Al LDHs were able to effectively remove chlorine species through both anion exchange and reformation mechanisms. There is considerable scope for future work concerning the removal of anionic chlorine species from aqueous solution by LDHs and thermally activated LDHs; however, the current lack of practical applications will undoubtedly discourage many researchers.

4. Removal of bromine species from aqueous solution by LDHs

4.1. Sources and toxicity of bromide (Br^-) and bromate (BrO_3^-): introduction

Bromine is an element that occurs naturally in some sources of water. Bromide (Br^-) is beneficial to human health at low levels but is toxic at high concentrations. Clinical symptoms of bromide toxicity (which are well documented due to its former use in medicine as a sedative and anticonvulsant) include the following: nausea, vomiting, abdominal pain, coma and paralysis [5]. Bromide has also been linked to a reduction in fertility in animal studies (Wistar rats) [5]. If bromide (Br^-) is present in a water source it can be oxidised to bromate (BrO_3^-) by ozonation and other methods of water disinfection or even sunlight irradiation [1,4,34]. Bromate was found to be both toxic and mutagenic in both *in vitro* and *in vivo* studies and was also carcinogenic in animal studies (F344 rats and B6C3F₁ mice) [1,4].

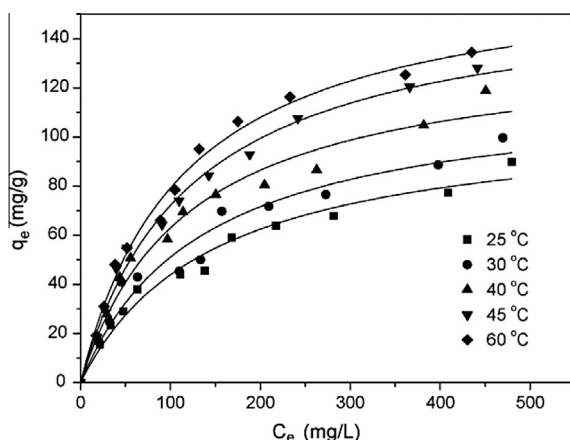


Fig. 6. Adsorption isotherms for chloride removal by Zn/Al LDHs by anion exchange. Figure reprinted with permission from Lv et al. [33].

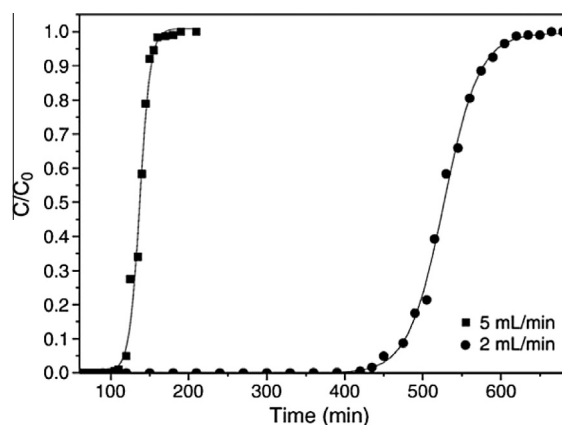


Fig. 7. Breakthrough curves for the fixed bed column method reported by Wu et al. [3] (experimental conditions: 1 g thermally activated LDH adsorbent, initial perchlorate concentration 100 mg/L. Figure reprinted with permission from [3].

The WHO has previously recommended that a health based guideline of 3 µg/L for bromate in drinking water should be implemented, however a provisional guideline value of 10 µg/L has been implemented due to current technical limitations [1,4]. The current provisional target of 10 µg/L is regarded as achievable using currently available technologies, however there is current no proven technologies able to achieve the WHO health based guideline of 3 µg/L [4]. Layered double hydroxides have been investigated as potential adsorbents for the removal of bromide and bromate from aqueous solutions under laboratory conditions [35–38].

4.2. Removal of bromide (Br^-) from aqueous solution by LDHs

Lv et al. [35] investigated the removal of bromide (Br^-) from water using Mg/Al LDHs and thermally activated Mg/Al LDHs. LDHs with interlayer carbonate were synthesised by conventional co-precipitation and thermally activated by calcination for 3 h in a muffle furnace at 500 °C. The uncalcined LDHs had the lowest bromide uptake of 27.5 mg/g with the bromide uptake capacity increases with the increase in calcination temperature to a maximum at 500 °C. Thermal activation temperatures above 500 °C caused partial decomposition of the LDH, reducing its ability to remove bromide through reformation [35]. The effect of adsorbent structure was investigated by comparing LDHs with different Mg:Al cation ratios. The highest bromide uptake of 94.0 mg/g was achieved using the thermally activated LDH with a Mg:Al ratio of 4:1 (Table 2). Lv et al. proposed that the large ionic radius of the bromide ion was more compatible with lower charge density of the cation layers in the thermally activated 4:1 Mg/Al LDH [35].

The optimum adsorbent dose of thermally activated LDH was 1.0 g/L with a bromide removal of 91.6%. Increasing the adsorbent dose beyond 1.0 g/L only had a small impact on bromide removal. This effect was consistent with heterogeneous surface sights on the thermally activated LDH [35]. An adsorption isotherm for the uptake of bromine by thermally activated LDH was plotted and investigated using both the Langmuir and Freundlich isotherm models. The Langmuir adsorption isotherm gave a better fit to the experimental data indicating that bromide sorption was a monolayer process (Fig. 8) [35]. Thermodynamic properties including Gibbs free energy (ΔG^0 , −21.31 kJ/mol), standard enthalpy of change (ΔH^0 , −17.96 kJ/mol) and standard entropy of change (ΔS^0 , −10.52 kJ/mol) were calculated. The negative ΔG^0 value confirms the spontaneity of bromide sorption process, while the negative ΔH^0 confirms its exothermic nature [35].

The kinetics of bromide sorption was investigated and found to fit the pseudo-second order model, indicating the rate of bromide uptake is limited by reaction of bromide with the thermally activated LDH [35]. Finally, the regeneration of the LDH adsorbent was investigated. The LDHs were regenerated by dispersal in sodium carbonate solution (0.1 M) for 6 h followed by filtration and washing. The recovered LDHs were thermally activated by calcina-

tion for 3 h in a muffle furnace at 500 °C. The LDH was able to undergo 5 regeneration cycles with only a small reduction in maximum bromide uptake capacity after each regeneration cycle. After 5 regenerations a bromide removal capacity of 89.7 mg/g was still observed (Table 2) [35].

Chitrakar et al. [39] investigated the removal of the bromide ion (Br^-) by Mg/Al, Mg/Fe and Zn/Al LDHs. Powder XRD patterns of all LDHs contained characteristic basal d003 and d006 peaks (basal spacing values are reported in Table 2). The 2:1 Mg/Al LDH appeared to contain an additional amorphous $\text{Al}(\text{OH})_3$ phase while Mg/Fe LDHs appeared to exhibit poorer crystallinity (Fig. 9) [39]. The synthesised LDHs were used to remove bromide (0.01 mmol/L) from solution. A 48–50% removal of bromide from solution was observed for the 3:1 and 4:1 Zn/Al LDHs, while the 2:1 Zn/Al LDH only removed 25% of the bromide in solutions under identical conditions [39]. Chitrakar et al. proposed that the stronger interactions between the charged layers exist in LDHs with high charge density (2:1). These interactions reduce the ability of the LDH to expand and accommodate large anions in the interlayer region. It was also proposed that the principal method of boron sorption in 2:1 LDHs was surface adsorption [39], however, the low bromide uptake of the 2:1 LDHs could also be the result of the high percentage of non-LDH phases in the samples (Table 2).

Thermally activated 3:1 and 4:1 Mg/Al LDHs and the 4:1 Mg/Fe LDH exhibited much high bromide uptake (90%). In contrast, the thermally activated Zn/Al LDHs exhibited lower bromide uptake than the uncalcined samples (14–17%) [39]. Chitrakar et al. attributed the low bromide uptake to an irreversible, partial decomposition of the LDHs during thermal activation indicating that the Zn/Al LDHs prepared in this study appear to have lower thermal stability than their Mg/Al or Mg/Fe counterparts [39]. Finally, the possibility of using a commercially available LDH (HT500, Tomita pharmaceuticals) for the removal of bromide from solution was investigated. Bromide uptake for the commercial LDH with and without thermal activation was 31% and 65% respectively. The lower bromide uptake was assigned to the charge density of the LDH, which was close to 3:1 [39] (see Table 3).

Prasanna et al. [36] investigated Zn/Al LDHs with interlayer bromide (Br^-) ions using powder XRD patterns and DIFFaX simulations. A LDH with a Zn:Al molar ratio of 2:1 was prepared by conventional co-precipitation under a nitrogen atmosphere [36]. Three binding sites which could accommodate bromide in the interlayer region have been identified in the literature, these are the 3b, 6c and 18 h sites (identified in Fig. 10). Prasanna et al. prepared DIFFaX simulations with bromide ions occupying only the 18 h positions as this is what has previously been reported in the literature [36]. The positions of key peaks in the simulated pattern correlated well with those in the experimental pattern with a better match obtained when stacking disorders were introduced into the model [36]. A simulation based on mixture of 80% $3R_1$ polytype and 20% of the less common $2H_1$ polytype gave the best match to the experimental pattern, however, the refined model was still unable to account for the intensity of the 015 reflection. A satisfactory match was achieved by introducing positional disorder of the interlayer bromide ions [36]. Prasanna et al. determined that bromide ions may also occupy some 6c sites. Bromide occupying the 6c sites had not been previously identified in the literature [36].

4.3. Removal of bromate (BrO_3^-) from aqueous solution by LDHs

Chitrakar et al. [34] investigated the removal of trace level bromate (BrO_3^-) from aqueous solution by thermally activated Mg/Al LDHs. Bromate uptake was carried out at room temperature using a batch method with an initial bromate concentration ranging from 0.02–0.78 µmol/L [34]. Thermal activation temperature had a significant impact on bromate removal, with no bromate removal

Table 2
The effect of Mg/Al ratio and the regeneration of the Mg/Al LDH adsorbent on bromide uptake reported by Lv et al. Data from [35].

| Thermally activated LDH (Mg:Al ratio) | Number or regeneration cycles | Bromide removal capacity (mg/g) |
|---------------------------------------|-------------------------------|---------------------------------|
| 2:1 | – | 55.8 |
| 3:1 | – | 74.0 |
| 4:1 | – | 94.0 |
| 4:1 | 1 | 91.6 |
| 4:1 | 2 | 91.3 |
| 4:1 | 3 | 90.7 |
| 4:1 | 4 | 90.9 |
| 4:1 | 5 | 89.7 |

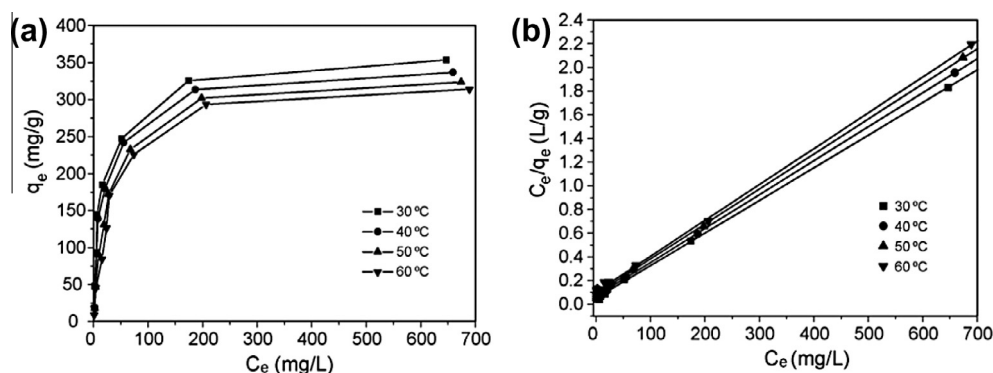


Fig. 8. Equilibrium isotherms (a) and Langmuir fitting (b) of bromide uptake by thermally activated Mg/Al LDHs. Figure reprinted with permission from Lv et al. [35].

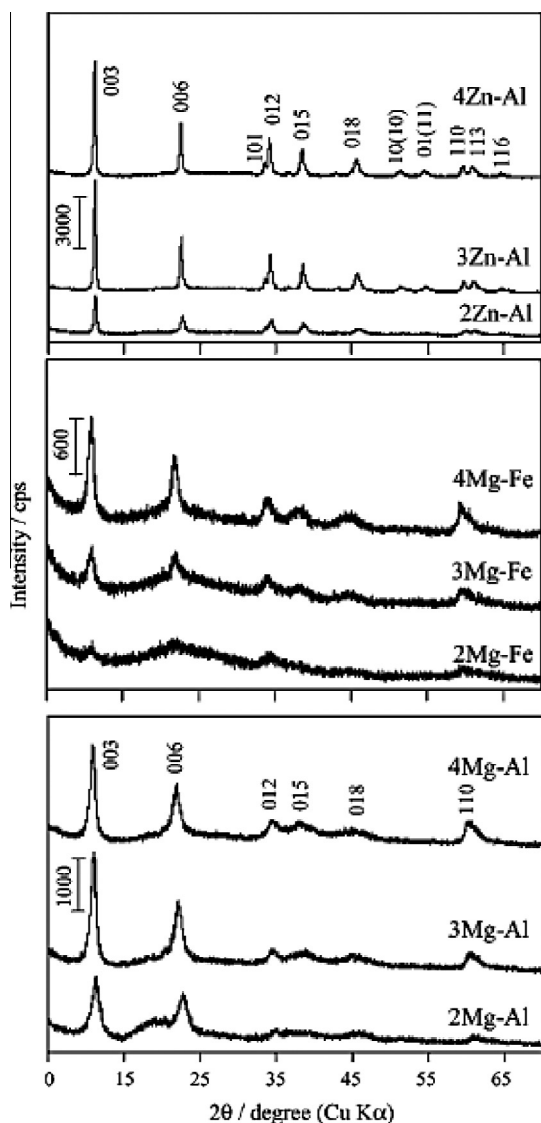


Fig. 9. Powder XRD patterns of LDHs prepared by Chitrakar et al. [39]. Reprinted with permission from: Chitrakar et al., Ind. Eng. Chem. Res., 2008, 47(14): p. 4905–4908. Copyright 2008 American Chemical Society.

observed for samples of LDH calcined at 300 °C. At 300 °C the thermal activation temperature was below the temperature required for the removal of interlayer anions [34]. LDHs thermally activated at 400 and 500 °C exhibited much higher bromate uptake. Bromate

concentration was reduced to less than 0.078 $\mu\text{mol/L}$ (from an initial concentration of 0.78 $\mu\text{mol/L}$) [34]. Although the initial bromate uptake was fast, equilibrium was not reached until 48–72 h and the initial solution pH (in the range of pH 4.0–10.0) was found to have little effect on bromate uptake by thermally activated LDHs [34]. The maximum dissolution of LDH adsorbent (thermally activated Mg/Al LDH prepared with interlayer carbonate) of 0.70 wt% occurred when the pH was less than 4.0 [34].

Bromate adsorption isotherms were plotted and compared to both the Langmuir and Freundlich isotherm models. A better fit was obtained with the Freundlich isotherm, suggesting that bromate sorption was either a heterogeneous or multilayer adsorption process [34]. Finally, the effect of competing anions on the removal of trace level bromate was investigated. Bromate sorption (with an initial bromate concentration of 0.78 $\mu\text{mol/L}$) was carried out in the presence of: chloride (Cl^-), nitrate (NO_3^-), sulphate (SO_4^{2-}) or carbonate (CO_3^{2-}) with concentrations varying from 0 to 1.0 mmol/L. Bromate uptake decreased significantly when the concentration of competing anions increased above 0.20 mmol/L [34]. Sulphate and carbonate had the greatest impact on bromate uptake, and this effect was attributed to the higher affinity LDHs exhibit for sulphate and carbonate anions [34].

Chitrakar et al. [37,38] investigated the removal of bromate by reduction to bromide by Fe/Al LDHs. Chitrakar et al. attempted to prepare LDHs with Fe:Al ratios of 1:1, 2:1, 3:1 and 4:1 by co-precipitation, however, only the 1:1 and 2:1 LDHs exhibited powder XRD patterns characteristic of a LDH structure. The powder XRD patterns of the LDHs with Fe:Al ratios of 1:3 and 1:4 appeared to be dominated by the pattern of the mineral goethite ($\text{FeO}(\text{OH})$) (Fig. 11). Thermogravimetry (TG) and differential thermal analysis (DTA) of the 1:1 and 1:2 LDHs revealed decomposition profiles typical of LDH structures while the 1:3 and 1:4 materials more closely resembled decomposition patterns of mixed oxides [37]. A 100% removal of bromate (initial concentrations 0.1 and 1.0 mmol/L) from mixed anion solutions containing: chloride (Cl^-), nitrate

Table 3

Selected properties of Mg/Al, Mg/Fe and Zn/Al LDHs reported by Chitrakar et al. [39]. Reprinted with permission from: Chitrakar et al., Ind. Eng. Chem. Res., 2008, 47(14): p. 4905–4908. Copyright 2008 American Chemical Society.

| LDH cation layer composition | LDH phase (%) | Basal spacing $d_{(003)}$ (nm) |
|------------------------------|---------------|--------------------------------|
| 2:1 Mg/Al | 62 | 0.785 |
| 3:1 Mg/Al | 69 | 0.799 |
| 4:1 Mg/Al | 91 | 0.812 |
| 2:1 Mg/Fe | 34 | 0.808 |
| 3:1 Mg/Fe | 68 | 0.808 |
| 4:1 Mg/Fe | 82 | 0.812 |
| 2:1 Zn/Al | 57 | 0.784 |
| 3:1 Zn/Al | 100 | 0.789 |
| 4:1 Zn/Al | 100 | 0.792 |

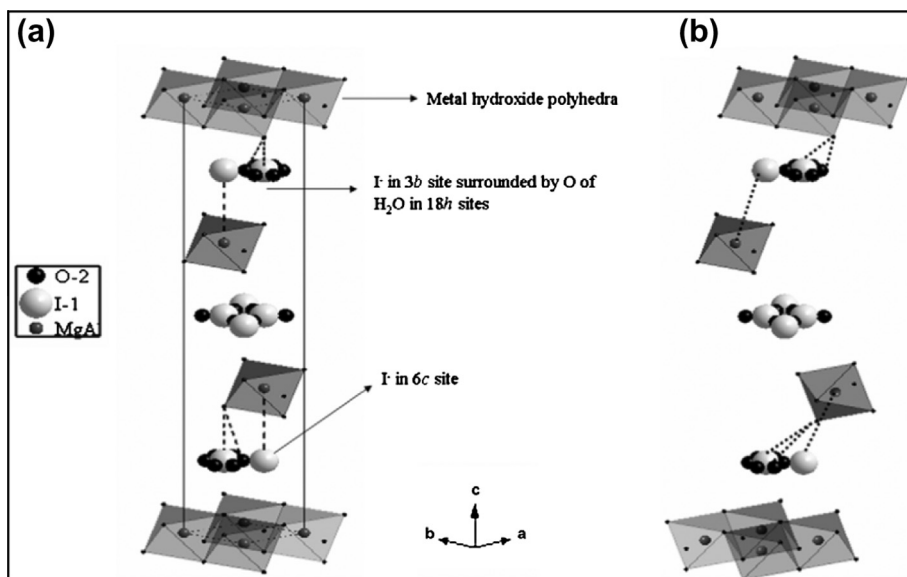


Fig. 10. A representation of the interlayer region of a Ma/Al LDH with interlayer iodide (I^-) ions as determined by Prasanna et al. (a) and the model after incorporation of turbostratic disorder (b). Figure reprinted with permission from [40].

(NO_3^-), dihydrogen phosphate ($H_2PO_4^-$) sulphate (SO_4^{2-}) and carbonate (CO_3^{2-}). The 2:1 Fe/Al LDH was found to be more effective at higher anion concentrations with 99% bromate removal observed (compared to 95% for the 1:1 Fe/Al LDH) with an optimum contact time of 2 h [37].

The amount of bromide released by the reduction reaction was smaller than expected. This effect was assigned to some adsorption of bromide on the outer surface of the LDHs. Bromate reduction was accompanied by a release of chloride into solution [37]. An optimum LDH dose of 0.6 g/L was required to completely remove bromate from a solution with an initial concentration of 100 $\mu\text{mol/L}$ [37]. Solution pH (in the range of pH 3–10) did not prevent complete bromate reduction; however, the rate of bromate reduction was increased at pH 3. The amount bromide liberated also increased with equilibrium pH. This effect was assigned to competition of OH^- groups competing with bromide for adsorption sites on the surface of the LDHs [37].

Chitrakar et al. [38] also investigated bromate reduction by Fe/Al LDHs with interlayer chloride and sulphate prepared by co-precipitation under a nitrogen atmosphere. Powder XRD patterns samples with Fe:Al ratios of 1:1 and 2:1 revealed the basal d003 and d006 reflections characteristic of LDH type structure [37,38]. Samples prepared with Fe:Al ratios of 3:1 and 4:1 did not appear to exhibit a LDH structure when investigated by powder XRD [38]. Bromate reduction was a rapid process. An almost 100% reduction of bromate from a 100 $\mu\text{g/L}$ solution was achieved in 1 h. Again, less than expected amount of bromide was released into solution and assigned to some adsorption of bromide on the outer surface of the LDHs. Bromate removal was investigated at various pH values ranging from 4.0 to 10.5 and complete bromate removal was achieved at all pH values investigated [38]. Chitrakar et al. also investigated the possibility of reusing the LDH. The LDH was washed and dried before re-use of the same sample of LDH. Removal efficiency decreased from 100% (for the initial run with fresh LDH) to only 19% after only 5 regeneration cycles (Table 4) [38].

4.4. Removal of bromine species from aqueous solutions by LDHs: conclusions and recommendations for future work

LDHs were able to effectively remove significant amounts of bromide from aqueous solution by anion exchange without

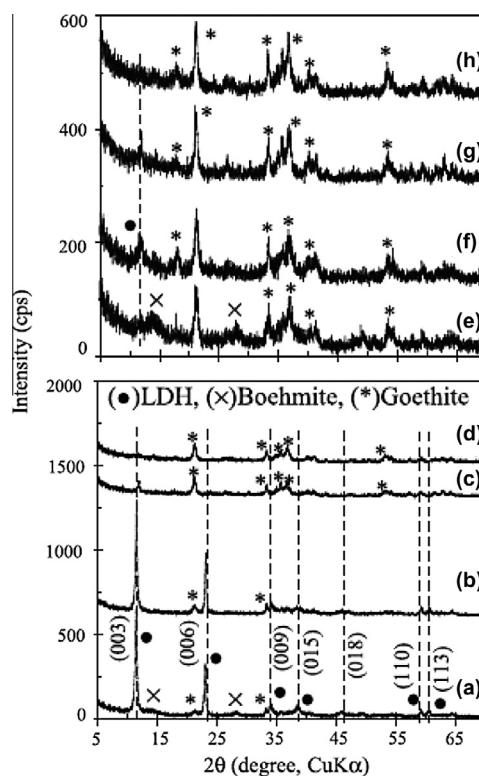


Fig. 11. Powder XRD of Fe/Al LDHs prepared by Chitrakar et al. (a and e) 1:1 Fe/Al LDH, (b and f) 2:1 Fe/Al LDH-2, (c and g) 3:1 Fe/Al LDH, (d and h) 4:1 Fe/Al LDH. Figure reprinted with permission from [37].

thermal activation. LDHs with low charge density (with divalent to trivalent cation ratios of 3:1 and 4:1) exhibited the greatest affinity for bromide (Br^-) ions. Thermal activation significantly increased bromide adsorption and was able to significantly reduce the concentration of bromate (BrO_3^-) at trace levels. Various Fe/Al LDHs were able to reduce bromate (BrO_3^-) to bromide (Br^-) in less than 1 h. The reduction of bromate is unlikely to permanently eliminate bromate contamination. Adsorption may be better suited

Table 4

Re-use of Fe/Al LDHs for the reduction of bromate reported by Chitrakar et al. [38].

| Number of uses of Fe/Al LDH | Bromate reduction (%) |
|-----------------------------|-----------------------|
| 1 | 100 |
| 2 | 99 |
| 3 | 89 |
| 4 | 72 |
| 5 | 19 |

to the removal of bromate because it may be able to immobilise and permanently remove bromate rather than converting it to bromide, which can then be re-oxidised to bromate under the correct conditions (bromide ions in water may have been the original cause of bromate contamination). Adsorption may also allow for at better recycling of the adsorbent, reducing the overall cost of bromate removal.

5. Removal of iodine from aqueous solutions by LDHs

5.1. Removal of iodine from aqueous solutions by LDHs: introduction

Iodine is an essential element for healthy thyroid development. The average daily intake of iodine required for optimal health is between 80 and 150 mg/day, however, a significant number of people around the world currently suffer from iodine deficiency. There is currently no WHO guideline standard for concentration of iodine or iodide in drinking, primarily due to a lack of reliable data on the effect of excess iodine intake [1]. Because of its antimicrobial properties, iodine can in fact be used for water disinfection, though this practice is only recommended for short term or emergency situations [1]. Though iodine is not toxic to humans, it does have several radioactive isotopes (radioisotopes) which are readily taken up by the body and concentrated in the thyroid (where iodine is required to produce a number of hormones) in the same manner as the predominant stable ^{127}I isotope. ^{131}I is a major by-product of uranium fission with a relatively short half-life of 8 days, and is a major public health hazard in the first weeks after nuclear accident (such as Chernobyl or Fukushima incidents) [1,7]. Another radioisotope of iodine, ^{129}I is far less common but is of some concern because of its extremely long half-life of several million years.

Methods for the removal of radioiodine from the environment and its safe long term storage must be developed if the operation and expansion of nuclear fission reactors as an alternative energy source to replace fossil fuels is to continue. A number of groups around the world have begun investigating LDHs (mainly of the Mg/Al hydrotalcite type) for the removal of various iodine species (including I^- and IO_3^-) from aqueous solution [6,7,13,41–43]. Iodine removal is complicated by the large number of iodine species which may be formed under different conditions. Diatomic iodine (I_2) has a low solubility in water, however, iodine readily reacts to form a number of soluble anions including: iodide (I^-), triiodide (I_3^-) and iodate (IO_3^-) [6,44].

5.2. Removal of iodide (I^-) from aqueous solution by LDHs

Some of the earliest work concerning the removal of iodide (I^-) from aqueous solutions by LDHs was carried out by Fetter et al. [7]. A number of Mg/Al hydrotalcite like LDHs were prepared by the co-precipitation or sol–gel methods with varying Mg:Al ratios and interlayer anions. Portions of the various LDHs were thermally activated at 773 K (approximately 500 °C) for 2 h [7]. Iodide sorption was carried out using sodium iodide solution (NaI) with an initial solution pH of 6. The iodide solutions were each treated with 50 mg sample of different LDHs for 24 h before separation by

centrifugation [7]. Fetter et al. unlike many subsequent groups used the ^{131}I isotope instead of the stable ^{127}I . The advantage of this technique was that the iodine concentration could be determined by γ -spectrometry [7]. Fetter et al. determined that the LDHs prepared by the conventional co-precipitation method were better iodide sorbents than those prepared by the sol–gel method. This effect was attributed to the larger crystallite size of the co-precipitated LDHs. Thermal activation greatly improved iodide uptake suggesting that Mg/Al LDHs have a lower affinity for iodide than carbonate, sulphate or nitrate. Thermal activation improved iodine uptake because it removed some of the existing interlayer anions which could not be displaced by iodide ions [7].

Liang and Li [41] investigated the removal of iodide ($^{127}\text{I}^-$) from aqueous solutions using Mg/Al LDHs. In addition to the effect of the cation ratio, Liang et al. also investigated the effect of thermal activation, LDH adsorbent dose, initial iodide concentration and the effect of competing anions. All LDHs were synthesised by the co-precipitation method and thermally activated LDHs were prepared by calcination of co-precipitated LDHs for 3 h in a muffle furnace at 500 °C [41]. The optimum Mg:Al ratio for maximum iodide sorption was 4:1 with an uptake capacity of 96.1 mg/g. Liang et al. proposed that 4:1 substituted LDH exhibited a greater affinity for iodide ions because of the large atomic radius of the iodide ion, which was better suited to the lower charge density of the 4:1 cation layers in the LDH [41]. The iodide uptake capacity increased with thermal activation temperature to a maximum of 96.1 mg/g at 500 °C. This temperature corresponded to the removal of the maximum number of interlayer anions with higher thermal activation temperatures causing a permanent decomposition of the cation layers which limited the material's ability to regenerate in the presence of the iodide solutions [41].

The effect of adsorbent dose on the sorption of iodide by thermally activated Mg/Al LDHs was investigated using a solution with an initial iodine concentration of 100 mg/L. The optimum dose of thermally activated LDH was 1.0 g/L resulting in a 96.5% iodide removal. Increasing the dosage beyond this point only had a small impact on iodide uptake. The overall maximum iodide uptake reported by Liang and Li. was 97.6% and was achieved using an adsorbent dose of 4.0 g/L [41]. Initial iodide concentration also had an effect on iodine uptake with iodide uptake capacity increasing with the equilibrium concentration of iodide until a maximum of 376 mg/g was reached [41]. Liang et al. were able to fit the experimental data to the Langmuir adsorption isotherm model and calculate Gibbs free energy using the Langmuir constant. The Gibbs free energy of the iodide sorption process was found to be negative (–23.8 kJ/mol) confirming the spontaneity of the iodide sorption process [41]. Finally, Liang et al. investigated the effect of competing anions on the sorption of iodide by thermally activated Mg/Al LDHs. Iodide uptake decreased as the concentration of competing anions (including: sulphate, phosphate and chloride) increased. This indicated that the LDHs exhibited greater affinity towards the competing anions investigated [41].

Prasanna et al. [40] investigated the poor stability of iodide intercalated LDHs and attributed it to various structural disorders. Mg/Al and Zn/Al LDHs with interlayer nitrate and iodide were prepared by co-precipitation and extensively characterised by powder XRD. Iodide (I^-) and bromide (Br^-) ions are strong X-ray scatterers and when intercalated into the interlayer of a LDH and can help mitigate the strong scattering of the cation layers, which usually swamp reflections from more weakly scattering anions [40]. DIF-FaX simulations of Mg/Al and Zn/Al LDHs with chloride, bromide and iodide anions in the interlayer region were prepared and compared to patterns obtained from the co-precipitated LDHs. In Mg/Al LDHs the intensity of the d003 and the 015 reflections decreased as scattering from the interlayer anions increased (moving down the periodic table from chloride to iodide) [40]. Similar results were

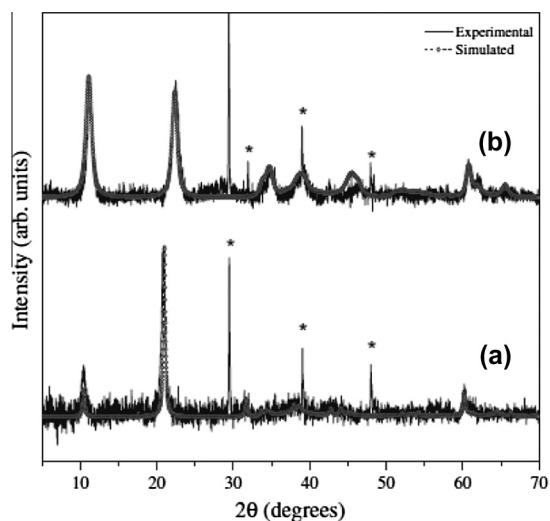


Fig. 12. comparison of powder XRD patterns of Mg/Al LDHs compared to DIFFaX simulated patterns incorporating positional disorders and turbostraticity with (a) iodide ions distributed in the 6c and 3b positions and (b) bromide ions distributed in the 18 h and 6c positions. Peaks marked * correspond to impurities (NaI and NaBr). Figure reprinted with permission from [40].

also observed for the Zn/Al LDH simulations, however, the d003 reflection did not completely disappear in the predicted pattern of the LDH with interlayer iodide. This effect was attributed to the stronger scattering of the Zn/Al cation layers [40]. Though the simulations were able to predict the significant d003 and d006 peaks with some accuracy, there were still some significant differences between the predicted and observed patterns, particularly in the 30–55 $2\theta^\circ$ region. This indicated that further refinement of the DIFFaX simulations was required to accurately predict the powder XRD patterns of the LDHs [40].

Non-uniform peak broadening is a phenomenon commonly observed in the powder XRD patterns of LDHs that is generally attributed to stacking disorders. The addition of stacking disorders to the models yielded poor matches to the actual powder XRD pattern [40]. The simulation which provided the best match to the experimental data was prepared using a random intergrowth of the two main LDH polytypes, the rhombohedral $3R_1$ (60%) and the hexagonal $2H_1$ (40%) along with a combination of positional disorder and turbostraticity (the random translation of adjacent layers) and that the structural disorders in Mg/Al LDHs could not be accounted for by stacking disorders alone (Fig. 12) [40]. Based on the best DIFFaX simulation iodide ions most likely occupy the 6c and 3b positions in the interlayer region (Fig. 10) [40]. The iodide is readily displaced from these sites by OH^- (the 3b site is particularly well suited to hydrogen bonding), which is a stronger hydrogen bond than iodide. This is consistent with experimental observations which have shown gradual leaching of iodide ions from LDHs [40].

5.3. Removal of Iodate (IO_3^-) from aqueous solution by LDHs

Toraishi et al. [42] compared iodate ($^{127}\text{IO}_3^-$) uptake by Mg/Al LDHs containing interlayer carbonate (CO_3^{2-}) and nitrate (NO_3^-) anions prepared by co-precipitation. Neither of the LDHs was thermally activated before iodate sorption, limiting the likely mechanism of anion uptake to anion exchange or surface adsorption. Anion sorption was carried out by immersing the LDHs (1.01 g) in potassium iodate solutions (between 1×10^{-4} and 2×10^{-1} M) [42]. Typically anion uptake is quantified by measuring the concentration of analyte before and after treatment by the LDH and calculating the difference. Toraishi et al. directly measured the iodate desorbed from the LDHs by inductively coupled

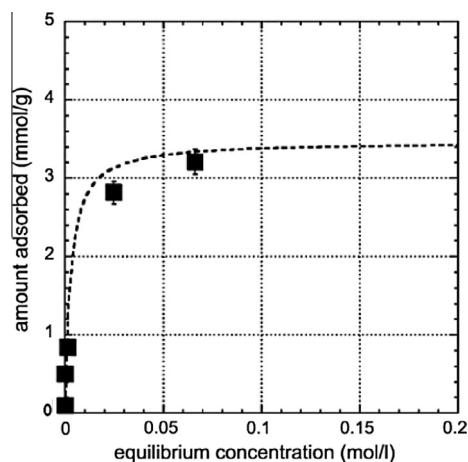


Fig. 13. Adsorption isotherm for iodate uptake by the Mg/Al LDH prepared with interlayer nitrate by Toraishi et al. Figure reprinted with permission from [42].

plasma optical emission spectroscopy (ICP-OES). Ion chromatography was used to confirm the absence of the iodide (I^-) anion [42].

Adsorption isotherms for both the carbonate and nitrate LDHs were plotted and compared to the Langmuir adsorption isotherm model (Fig. 13). The process of iodate uptake by the nitrate LDH could be described by the Langmuir model indicating that iodate sorption was most likely a monolayer process. The maximum adsorption capacity of the nitrate LDH was calculated to be 3.7 meq/g [42]. Powder XRD showed a slight expansion of the LDH interlayer sufficient to accommodate iodate anions, suggesting that the mechanism of iodate sorption involved anion exchange [42]. Powder XRD patterns also showed reflections characteristic of a LDH structure up to an iodate concentration of 1×10^{-3} M. At higher iodate concentrations (0.05 and 0.01 M) the d003 and d006 reflections were too weak to measure the interlayer spacing and the pattern appeared almost amorphous. Toraishi et al. concluded that iodate was intercalated horizontally into the interlayer region and that a high degree of this intercalation reduced the crystallinity of the LDH [42].

In contrast to the nitrate LDH, the carbonate LDH did not fit a single Langmuir isotherm model (Fig. 14). Instead of attempting to use another model (such as the Freundlich isotherm) Toraishi et al. fitted the data using two consecutive Langmuir isotherms. The maximum adsorption capacities of the two Langmuir isotherms were calculated as 9.1 meq/g and 3.4 meq/g with an estimated error of 10% [42]. The carbonate LDH showed a more complex and faster adsorption process than the nitrate LDH. It was proposed that sorption of iodate by the carbonate LDH occurred through surface adsorption alone (as would be expected for a carbonate LDH without thermal activation), however the 100% uptake iodate in 200 h by this mechanism (almost 450 h were required for the nitrate LDH) is surprising [42]. The outer surfaces of the LDHs should have been characterised to determine if there was any significant difference in surface size or morphology that may have affected iodate adsorption. Powder XRD showed a characteristic LDH pattern for all samples of the carbonate LDH. An additional potassium iodate phase was observed in LDHs recovered from treatment in solutions with an initial iodate concentration of 0.10 M, indicating that a crystalline potassium iodate phase formed on the outer surface of the LDH [42].

As previously mentioned, desorption studies are extremely important if the adsorbed anion is to be stored for prolonged periods. In this case the desorption studies also highlighted the different mechanisms of anion sorption of the nitrate and carbon-

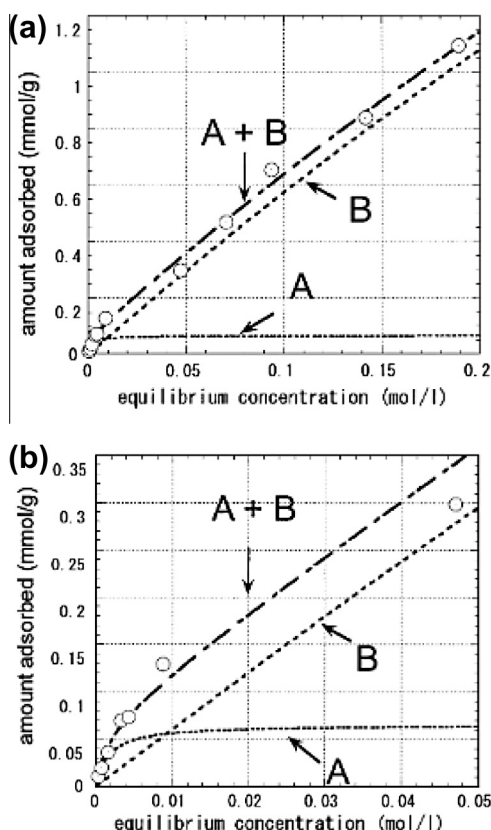


Fig. 14. Adsorption isotherms for iodate uptake by the Mg/Al LDH prepared with interlayer carbonate by Toraishi et al. Figure reprinted with permission from [42].

ate LDHs. Iodate was desorbed from the carbonate LDH after immersion in deionised water indicating that surface adsorption predominated in this sample [42]. In contrast, only approximately 10% of the iodate taken up was desorbed from the nitrate LDH under the same conditions. Complete exchange of iodate was only achieved by immersion in solutions containing nitrate and chloride anions, thereby confirming that the main method of iodate uptake was anion exchange [42].

Kulyukhin et al. [6] investigated the removal of both iodate and iodide from water using Mg/Al LDHs and thermally activated Mg/Al LDHs. Kulyukhin et al. used $^{131}\text{I}^-$ and $^{131}\text{IO}_3^-$ solutions ($1 \times 10^{-5} \text{ M}$) prepared from stock Na^{131}I . Iodine concentration was determined by γ -spectrometry using a multichannel analyser with a Ge–Li semiconducting detector [6]. The 3:1 Mg/Al LDH adsorbents were prepared with interlayer carbonate or nitrate by conventional co-precipitation and a thermally activated LDH was prepared by calcination of the carbonate LDH for 2 h at 820 K (approximately 550 °C).

Kulyukhin et al. found that Mg/Al LDHs prepared with interlayer carbonate or nitrate were not able to remove significant amounts of iodate or iodide from water by anion exchange or surface adsorption. These results appear to directly contradict the earlier findings of Toraishi et al. who determined that Mg/Al LDHs with interlayer carbonate or nitrate were able to remove iodate by a surface adsorption and anion exchange respectively [42]. It is possible that this result may be due to different experimental conditions or morphologies of the LDH adsorbent with Kulyukhin et al. proposing that low iodine uptake observed in their experiments may have been due to steric hindrance [42]. The thermally activated Mg/Al LDH was much more effective for the removal of iodide and iodate anions from solution [42].

5.4. Removal of iodine from real world optoelectronic wastewater

Optoelectronic wastewater is generated in large quantities during the production of thin film liquid crystal displays and typically contains high levels of both boron and iodine [45]. The antimicrobial properties of iodine typically limit the effectiveness of biological treatment processes; therefore the removal of iodine from the wastewater may make it easier to treat. Kentjono et al. [45] attempted to use a 2:1 Mg/Al LDH (empirical formula: $\text{Mg}_{0.66}\text{Al}_{0.34}(\text{OH})_2(\text{NO}_3)_{0.34} \cdot 0.52\text{H}_2\text{O}$) prepared by co-precipitation to simultaneously remove both iodine and boron from a sample of optoelectronic wastewater collected from a manufacturing facility in Tainan, Taiwan [45]. Chemical analysis of the wastewater indicated that it contained the following: iodine (973.98 mg/L), boron (753.01 mg/L), carbon (16.06 mg/L), chloride (14.58 mg/L), and zinc (7.69 mg/L) [45]. The effect of pH on iodine uptake was investigated by adjusting the solution pH by careful addition of either sodium hydroxide or nitric acid. A maximum iodine uptake capacity of 10.1 mg/g occurred at pH 9.2, indicating that iodine and boron could be removed simultaneously by the Mg/Al LDH [45]. Boron sorption was further investigated by plotting an adsorption isotherm which was compared to the Langmuir adsorption isotherm model, however, iodine sorption was not investigated in the same manner [45]. Kentjono et al. concluded by proposing that iodine was removed through adsorption onto external surfaces rather than anion exchange [45].

5.5. Removal of iodine species from aqueous solutions by LDHs: conclusions and recommendations for future work

While LDHs generally show low affinity for iodide (I^-), thermally activated LDHs have shown some promise for the removal of iodine contaminants (particularly the iodate, IO_3^- ion) from water with LDHs with low charge density (Mg:Al ratio of 4:1) showed the greatest affinity for iodide. Further investigation into the sorption of iodine and iodide contaminants by LDHs and thermally activated LDHs is required. As is the case with many other anions, the vast majority of experiments concerning the removal of iodide and iodate have been carried out using Mg/Al LDH adsorbents. Other cation combinations (such as Zn/Al and Mg/Fe) should be also investigated.

6. Overall conclusions

LDHs and thermally activated LDHs have shown potential for the removal of anions and oxyanions of the halogen elements in controlled laboratory scale experiments. The structure of LDHs had a significant impact on anion uptake. The optimal $\text{M}^{2+}:\text{M}^{3+}$ ratio was influenced by the nature of the anion and is summarised in Table 5. In general LDHs with high charge density exhibited greater affinity for anions with high charge density (F^- , Cl^- , ClO_4^-

Table 5

Optimum LDH divalent to trivalent ratio reported for the removal of anionic halogen species.

| Anion | Optimum LDH cation ratio ($\text{M}^{2+}:\text{M}^{3+}$) | References |
|------------------|--|------------|
| F^- | 2:1 (Mg/Al) | [12] |
| BF_4^- | 4:1 (Mg/Al) ^a | [29] |
| Cl^- | 2:1 (Zn/Al) | [33] |
| ClO_4^- | 2:1 (Zn/Al) | [3] |
| Br^- | 4:1, 3:1 (Mg/Al, Zn/Al) | [35,36,39] |
| BrO_3^- | 2:1 (Mg/Al, Fe/Al) | [34,37,38] |
| I^- | 4:1 (Mg/Al) | [7,41] |
| IO_3^- | 3:1 (Mg/Al) ^a | [42] [6] |

^a This is the only $\text{M}^{2+}:\text{M}^{3+}$ ratio reported for this anion.

and BrO_3^-), while LDHs with low charge density were better for the removal of anions with low charge density (Br^- and I^-). This was generally attributed to either the compatibility of the charge density of the adsorbent and adsorbate or differences in the surface morphology of the LDHs.

The mechanism of anion uptake depended on the nature of both the adsorbent and adsorbate. LDHs were able to remove some target anion species through anion exchange and surface adsorption, however thermal activation improved anion uptake. Thermally activated LDHs were able to significantly reduce the concentration of all anions reported laboratory scale experiments. In general optimum anion sorption occurred under slightly acidic conditions (typically pH 6.0) where LDHs are still stable (does not dissolve) there were fewer hydroxide anions to compete with the adsorbate for binding sites. The effect of competing anions on the uptake of anions and oxyanions of halogen elements was significant. LDHs typically exhibited lower affinity for halide ions than other anions with multiple charges including carbonate, phosphate and sulphate. The presence of these ions was found to decrease the uptake of the target anion. A very limited number of studies concerning the removal of fluoride and perchlorate in a continuous flow system utilising fixed bed columns packed with LDH adsorbents have also been carried out. Adsorption capacity of the columns at breakpoint was always lower than that reported for the corresponding batch methods with lower flow rates providing better results as expected.

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References

- [1] Guidelines for Drinking-water Quality, fourth ed. WHO Press, World Health Organization: Geneva, Switzerland, 2011.
- [2] J. Fawell et al., Fluoride in Drinking-water, Published on behalf of the World Health Organization by IWA Publishing, Alliance House, 12 Caxton Street, London SW1H 0QS, UK, 2006.
- [3] X. Wu et al., *Desalination* 256 (1–3) (2010) 136–140.
- [4] A. Bathija, Bromate in Drinking-water, Background document for development of WHO Guidelines for Drinking-water Quality, Springer, Berlin, 2004.
- [5] J. Cotruvo, Bromide in Drinking-water, Background Document for development of WHO Guidelines for Drinking-water Quality, Springer, Berlin, 2009.
- [6] S.A. Kulyukhin et al., *Radiochemistry* 49 (5) (2007) 499–503.
- [7] G. Fetter et al., *J. Radioanal. Nucl. Chem.* 221 (1997) 63–66.
- [8] V. Rives, *Mater. Chem. Phys.* 75 (2002) 19–25.
- [9] R.L. Frost, S.J. Palmer, H.J. Spratt, *J. Therm. Anal. Calorim.* 95 (1) (2009) 123–129.
- [10] R.L. Frost, J.M. Bouzaid, W.N. Martens, *J. Therm. Anal. Calorim.* 89 (2) (2007) 511–519.
- [11] K.L. Erickson, T.E. Bostrom, R.L. Frost, *Mater. Lett.* 59 (2–3) (2004) 226–229.
- [12] L. Lv et al., *J. Hazard. Mater.* 133 (1–3) (2006) 119–128.
- [13] V. Rives, *Layered Double Hydroxides: Present and Future*, Nova Science Pub. Inc., New York, 2001.
- [14] Sara J. Palmer, A. Soisonard, Ray L. Frost, *J. Colloid Interface Sci.* 329 (2) (2009) 404–409.
- [15] P. Atkins, J. De Paula, *Atkins' Physical Chemistry*, Oxford University Press, 2006.
- [16] M.L. Jiménez-Núñez, M.T. Olguín, M. Solache-Ríos, *Sep. Sci. Technol.* 42 (16) (2007) 3623–3639.
- [17] M.L. Jiménez-Núñez, M. Solache-Ríos, M.T. Olguín, *Sep. Sci. Technol.* 45 (6) (2010) 786–793.
- [18] Y. Liu, R. Naidu, H. Ming, *Geoderma* 163 (1–2) (2011) 1–12.
- [19] Sara J. Palmer et al., *J. Colloid Interface Sci.* 342 (1) (2010) 147–154.
- [20] S.J. Palmer, B.J. Reddy, R.L. Frost, *Spectrochim. Acta Part A* 71A (5) (2009) 1814–1818.
- [21] W.-T. Tsai et al., *Bioresour. Technol.* 99 (6) (2008) 1623–1629.
- [22] V.K. Gupta, I. Ali, V.K. Saini, *Water Res.* 41 (15) (2007) 3307–3316.
- [23] V.K. Gupta, S. Agarwal, T.A. Saleh, *Water Res.* 45 (6) (2011) 2207–2212.
- [24] A.K. Jain et al., *Sep. Sci. Technol.* 38 (2) (2003) 463–481.
- [25] H. Wang et al., *Appl. Clay Sci.* 35 (1–2) (2007) 59–66.
- [26] L. Lv, *Desalination* 208 (1–3) (2007) 125–133.
- [27] D.P. Das, J. Das, K. Parida, *J. Colloid Interface Sci.* 261 (2002) 213–220.
- [28] T. Zhang et al., *Synthesis of Li–Al layered double hydroxides (LDHs) for efficient fluoride removal*, *Ind. Eng. Chem. Res.* (2012).
- [29] T. Yoshioka et al., *Chemosphere* 69 (5) (2007) 832–835.
- [30] S.K. Yun, T.J. Pinnavaia, *Chem. Mater.* 7 (2) (1995) 348–354.
- [31] M. Sheffer (Ed.), *Chloride in Drinking-Water*, Background Document for Development of WHO Guidelines for Drinking-Water Quality, World Health Organization, Geneva, Switzerland, 2003.
- [32] *Drinking Water: Regulatory Determination on Perchlorate*, Environmental Protection Agency (EPA), 2011, pp. 7762–7767.
- [33] L. Lv et al., *J. Hazard. Mater.* 161 (2–3) (2009) 1444–1449.
- [34] R. Chitrakar et al., *Ind. Eng. Chem. Res.* 50 (15) (2011) 9280–9285.
- [35] L. Lv et al., *J. Hazard. Mater.* 152 (3) (2008) 1130–1137.
- [36] S.V. Prasanna et al., *Clays Clay Miner.* 57 (1) (2009) 82–92.
- [37] R. Chitrakar et al., *J. Colloid Interface Sci.* 354 (2) (2011) 798–803.
- [38] R. Chitrakar et al., *Sep. Purif. Technol.* 80 (3) (2011) 652–657.
- [39] R. Chitrakar et al., *Ind. Eng. Chem. Res.* 47 (14) (2008) 4905–4908.
- [40] S.V. Prasanna, P.V. Kamath, C. Shivakumara, *J. Colloid Interface Sci.* 344 (2) (2010) 508–512.
- [41] L. Liang, L. Li, *J. Radioanal. Nucl. Chem.* 273 (1) (2006) 221–226.
- [42] T. Toraisi, S. Nagasaki, S. Tanaka, *Appl. Clay Sci.* 22 (1–2) (2002) 17–23.
- [43] F.L. Theiss et al., *Desalination Water Treatment* 39 (2011) 166–175.
- [44] G. Schmitz, *Physical Chemistry Chemical Physics* 1 (8) (1999) 1909–1914.
- [45] L. Kentjono et al., *Desalination* 262 (1–3) (2010) 280–283.