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Zinc aluminium layered double hydroxides for the removal of iodine and iodide from aqueous solutions

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ABSTRACT

^{129}I is a radioactive isotope of iodine that is readily absorbed by the body. In this paper we investigated the potential of a 3:1 Zn/Al layered double hydroxide (LDH) as a sorbent for the removal of iodine and iodide from water. Synthetic $Zn_6Al_2(OH)_{16}(CO_3)\cdot 4H_2O$ was prepared by the co-precipitation before thermal activation. The LDH was treated with solutions containing iodide and iodine. It was found that iodine could be more easily removed from solution than iodide. Powder X-ray diffraction revealed the destruction of the LDH structure during thermal activation and the successful reformation of a similar LDH material after treatment with the iodide or iodine solution. Thermal decomposition of all samples studied by thermogravimetry appeared to be similar. A new decomposition mechanism similar to one previously described in the literature was proposed for the Zn/Al LDH. The total mass loss of samples treated with iodide and iodine was significantly lower than that of the original LDH indicating that iodine species may form non-removable anions when intercalated into the LDH structure. Evolved gas mass spectrometry failed to detect any iodine species lost as gases during the decomposition of iodide treated LDH however, small quantities of iodine species were observed during decomposition of samples treated with iodine solution.

Keywords: Iodine; Iodide; Radioiodine; Layered double hydroxide; Hydrotalcite; Water purification

1. Introduction

Iodide is an essential element necessary for normal thyroid development. The estimated dietary requirement of iodine for adults is between 80–150 µg/d. Though is currently no WHO standard for iodine or iodide in drinking water several unstable isotopes of iodine are known to exist including ^{129}I which is a radioactive isotope of iodine produced as a by-product of uranium fission [1]. Radioactive iodine (also known as radioiodine) is readily absorbed by the body resulting in a detrimental effect on human health.

In light of the recent incident at the Fukushima nuclear power station in Japan developing materials for the safe removal and storage of radioactive iodine species from air and water is a priority especially if atomic energy is to be used as a replacement for fossil fuels in the near future. Layered double hydroxides (LDHs) are a group of naturally occurring and synthetic clay minerals that exhibit a number of useful properties. Also known as anionic clays or hydrotalcite like materials, LDHs are based on the brucite ($Mg(OH)_2$) structure in which some

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divalent layer cations are replaced with trivalent cations (Al^{3+} in the case of hydrotalcite one of the first minerals of this type to be discovered) [2–13].

A useful property exhibited by LDHs is known as the reformation (or memory) effect. Calcination at elevated temperatures in the region of 300–500°C results in the elimination of interlayer water, anions and the hydroxyl groups resulting in a mixed metal oxide. This process is usually referred to as thermal activation. It is sometimes possible to restore the original LDH structure by immersion in water containing dissolved anions. Anions present in the solution as well as OH^- from water are incorporated into the new LDH structure. LDHs have been successfully used to remove numerous undesirable anions from solutions including: chloride, fluoride, selenite, nitrate and numerous other anions [14–25]. However if a LDH is thermally activated at too high a temperature the material may be permanently decomposed to a mixed metal oxide. As mixed metal oxides do not exhibit reformation anion sorption efficiency is reduced.

Other groups have previously investigated the removal of iodine species from aqueous solution using Mg/Al LDHs. Early work by Fetter et al. determined that sorption of iodide required thermal activation of the hydrotalcite with very little iodide removal occurring in non-thermally activated samples [16]. This indicated that hydrotalcites have a lower affinity for iodide than carbonate or sulphate which were the interlayer anions present in the LDHs used.

Removal of iodide using Mg/Al LDHs was also investigated by Liang et al. [21]. This paper reported up to 97.6% iodide removal using a Mg/Al LDH (4.0 g/l). The effect of LDH structure, LDH dosage, initial iodide concentration and the presence of competing anions were all examined. The optimum cationic ratio for the LDH adsorbent was found to be 4:1 with an uptake capacity of 96.1 mg/g. This was attributed to the large atomic radius of the iodide ion having grater affinity for the lower charge density of the 4:1 substituted LDH. Thermal activation was investigated and found to improve iodide uptake. Uptake of iodide increased with thermal activation temperature with a maximum calcination temperature of 500°C. The optimum dose of LDH was found to be 1.0 g/l resulting in a 96.5% removal of iodide ions. Increasing the dosage beyond this point only produced minor improvements. The effect of initial iodide concentration was investigated and it was found that the uptake capacity of increases with the equilibrium concentration of iodide. The maximum uptake capacity was found to be 376 mg/g. The Langmuir model was able to be applied to the experimental data to yielding an acceptable fit. Using the Langmuir constant it was possible to calculate the Gibbs free energy of the process which was found to be −23.8 kJ/mol confirming the spontaneity of the process. Finally the effect of competing anions on the sorption of iodide was tested. The percentage removal of iodide was to decrease as the concentration of competing anions increased. This was most likely due to the low affinity of LDHs for iodide and the grater affinity for other anions.

Kulyukhin et al. investigated the removal of iodide as well as the iodate anions (IO_3^-) from water using Mg/Al LDHs [22]. When iodine is dissolved in water it partially disproportionates into numerous species including I^- and IO^-. IO^- upon reacting with itself decomposed to IO_3^- and I^-. It was proposed that I^- and IO_3^- are the major iodide species present in water contaminated with radioiodine [22]. It was determined that LDHs were not able to remove IO_3^- and I^- by anion exchange confirming the results of Fetter et al. [16]n. Thermally activated LDHs were found to be more effective at removing the IO_3^- and I^- anions from solution.

In this work we have investigated the removal of iodide and iodine in the form of $K^{127}I$ and $^{127}I_2$ from water using a synthetically prepared thermally activated (TA) Zn/Al LDH material as a sorbet. To our knowledge no results for the sorption of iodine species by Zn/Al LDHs have been previously reported in the literature.

2. Reagents

The stable ^{127}I isotope was chosen for these preliminary experiments for safety reasons. The potassium iodate used was LR grade. All other reagents used were AR grade. All reagents were used as received with no additional purification or pre-treatment.

3. Experimental procedure

3.1. Synthesis of Zn/Al LDH

A quantity of 3:1 zinc/aluminium layered double hydroxide (Zn-LDH) was prepared by the co-precipitation method. The mixed metal solution was prepared by dissolving zinc chloride (60.36 g) and aluminium chloride hexahydrate (183.33 g) in ultrapure water (1000 cm^3). The caustic solution was prepared by dissolving sodium hydroxide (80.05 g) and sodium carbonate (170.00 g) in ultrapure water (1000 cm^3). The caustic solution (1000 cm^3) was added drop wise to the mixed metal solution (1000 cm^3) with constant stirring. As the solutions were combined the LDH formed as a white precipitate. The pH of the mixture was not recorded. The mixture was left to stir for approximately two hours before it was separated by vacuum filtration. The solid LDH (169.03 g) was collected and dried overnight in an oven at 80°C then ground with a mortar and pestle.

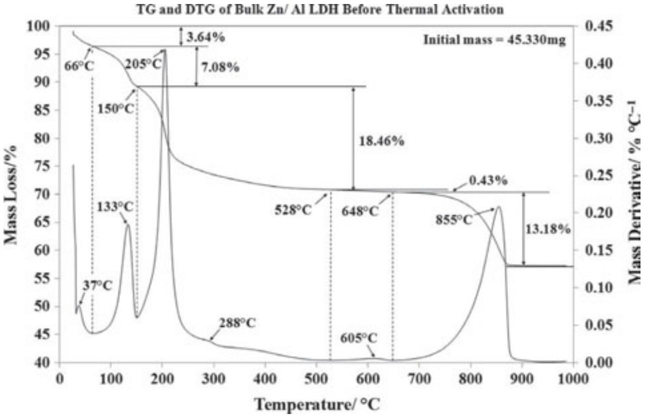

Fig. 1. TG and DTG curves of Zn/Al LDH before thermal activation or absorption experiments.

3.2. Thermal activation and iodine sorption

Using the results of the thermogravimetric analysis presented in Fig. 1 a thermal activation (TA) temperature of 280°C was chosen. This temperature was chosen as it was well above the major mass loss at 217°C but still low enough to allow for reformation of the LDH structure. TA was carried out in a furnace which reached a maximum temperature of 371°C before slowly decreasing to approximately 310°C over one hour. A mass loss of 27.09% was observed after thermal activation (ATA). This corresponded well to the mass loss observed during TG of the sample. The LDH was also observed to undergo a colour change during TA, changing from white to a light green colour.

Iodide sorption was investigated using samples of TA-Zn/Al LDH. Initial experiments were carried out to determine the mass of LDH required to completely remove iodide or iodine from solution. Various combinations of 1, 2 and 3 g samples of LDH were treated with an iodide solution (0.09 M) prepared by dissolving potassium iodide in ultra pure water and a iodine solution prepared by dissolving potassium iodide (approximately 0.56 g) and potassium iodate (approximately 0.14 g) in deionised water (20 ml). Three drops of concentrated hydrochloric acid was then added causing iodine to form in solution.

Results were quantified by treating approximately 1 g samples with the same iodide solution described above. The mixture was allowed to stir for 30 min before separation by vacuum filtration. The liquid samples were collected and treated with excess potassium iodate and three drops of concentrated hydrochloric acid. The concentration of iodine was determined by thiosulphate titrations using standardised sodium thiosulphate solution (0.029 M) and soluble starch as an indicator. The solid samples were collected and dried for analysis by Powder XRD and TG.

Approximately 1 g samples of LDH were also treated with the same iodine solution described above. TA-Zn/Al LDH was added and allowed to stir for 30 min. The mixture was separated by vacuum filtration before the solid samples were dried and retained for further analysis. The liquid samples were titrated directly with standard sodium thiosulphate solution to determine the concentration of iodine present. The LDH was observed to change colour to a slightly darker gray yellow colour after sorption of iodide and a faint yellow brown after sorption of iodine. More detailed experiments were carried out to quantify the removal of both iodide and iodine from solution. Approximately 1 g samples of Zn/Al LDH were added to solutions of iodide and iodine and stirred for 30 min, as described in Tables 1 and 2. The mixture was once again separated by vacuum filtration the filtrate was collected and immediately titrated as described previously. All measurements were carried out in triplicate.

The sodium thiosulphate solution used for the titrations was standardised by titration with iodine. The concentration of the thiosulphate solution was found to be 0.0292 mol/l. Detailed calculations are available in the supplementary materials document.

3.3. Characterization of synthetic hydrotalcite samples

Samples of synthesised Zn-LDH before and after thermal activation were characterised by powder X-ray diffraction (XRD) as well as samples collected after treatment with iodide and iodine solution. X-ray diffraction patterns were collected using a Philips X'pert wide angle X-ray diffractometer, with Cu Kα radiation (1.54052 Å).

Thermogravimetric analysis (TG) was performed on samples of Zn-LDH before thermal activation and samples treated with iodide and iodine solution. A TA® Instruments incorporated high resolution thermogravimetric analyser (series Q500) was used for thermal analysis experiments with a flowing nitrogen atmosphere (40 cm^3/min). The samples were placed in an

Table 1
Results of the titration of iodide solution after treatment with Zn/Al LDH

Titration number	Initial concentration of KI Solution (M)	Mass of Zn/Al LDH (g)	Volume of $S_2O_3^{2-}$ solution required (ml)
1	0.089	1.0381	17.2
2	0.089	1.092	19.8
3	0.089	1.0714	18.8
Average	**0.089**	**1.0816**	**18.6**

Table 2

Results of the titration of iodine solution after treatment with Zn/Al LDH

Titration number	Mass of Zn/Al LDH (g)	Mass KI measured (g)	Mass KIO_3 measured (g)	Solution volume (ml)	Volume of thiosulphate (ml)
1	1.03	0.5836	0.1412	20	6.0
2	1.03	0.5870	0.1424	20	6.8
3	1.04	0.5675	0.1428	20	6.5
Average	**1.03**	**0.5794**	**0.1421**	**20**	**6.4**

open platinum pan and heated from room temperature at a rate of 2.50°C/min to a maximum temperature of 1000°C. TG and DTG curves were obtained. After initial examination of the results the thermogravimetric analysis was repeated to allow for evolved gas mass spectrometry. It was hoped this technique would provide additional information on the thermal decomposition of the samples. The TA® Instruments incorporated high resolution thermogravimetric analyser (series Q500) used in earlier experiments was coupled to a Balzers (Pfeiffer) mass spectrometer for gas analysis. The mass spectrometer was configured to analyse only selected gases including carbon dioxide, nitrogen/ carbon monoxide, oxygen, water and numerous iodine species including I, I_2, IO, IO_2, IO_3, IO_4, and IO_5.

4. Results and discussion

4.1. Iodine and iodide sorption

It was found that three 3 g applications of LDH were required before no iodide was observed in solution However, only two 3 g applications were required to completely remove iodine from solution. More detailed results for the sorption of iodide and iodine sorption are presented in Table 1 and Table 2 respectively. It was found that treatment of 20 ml of the iodide solution with an initial concentration of 0.088 mol/l with approximately 1 g of Zn/Al LDH resulted in a 36.8% removal. The removal of iodine solution was found to be more effective with 99.5% removal from 20 ml of solution with an initial concentration of 0.1 mol/l using approximately 1 g of Zn/Al LDH.

It has been established iodine reacts with water resulting in a number of anions which may subsequently react further to give a range of possible iodine species in solution [26]. It is possible that these equilibrium reactions may result in the formation of an anion that the LDH adsorbent material has a high affinity for. Initially only a small amount of the anions are required. As the anion is removed by the adsorbent, the equilibrium will shift to favour the generation of more of the anion.

4.2. Powder XRD of Zn LDH

Powder XRD was carried out on a sample of the LDH before thermal activation and is presented in Fig. 2. Major peaks in the pattern obtained from a sample of the LDH before thermal activation or treatment with anion solutions correspond to an accepted reference for a Zn/Al LDH (00-038-0486). However, distinct shifts in

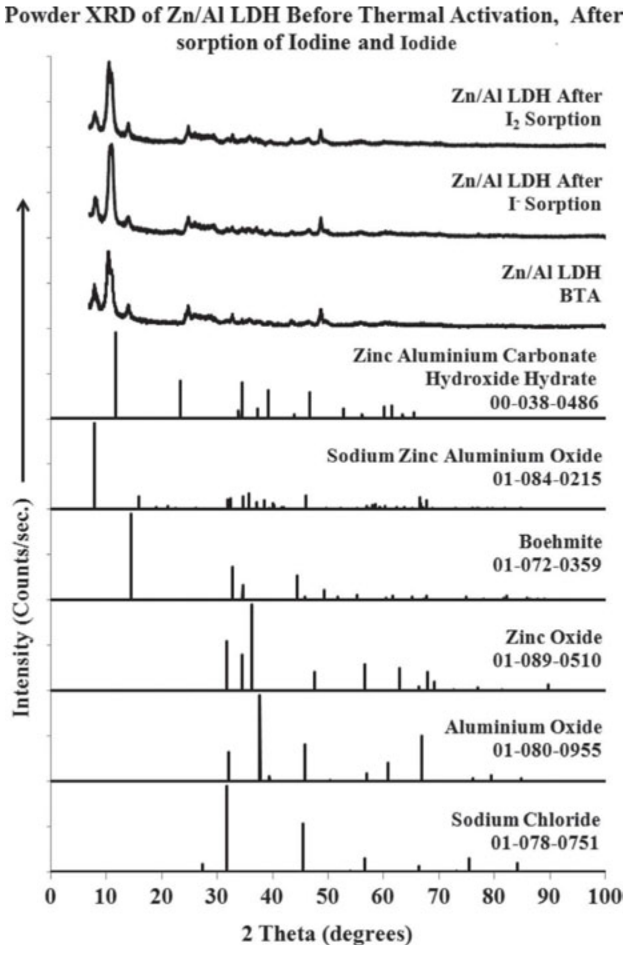

Fig. 2. Powder XRD pattern of Zn/Al LDH before thermal activation and after reformation in iodide or iodine solution with references.

peak positions are observed indicating differences in the layer spacing. The d_{003} spacing was found to be 8.07Å which is within the accepted range for a LDH structure. Additional phases such as sodium zinc aluminium oxide, boehmite, zinc oxide and aluminium oxide also appear to be present. Significant peaks that correspond to sodium chloride, a major by-product of the synthesis, was not observed in the pattern indicating that it was successfully removed during the washing process.

Powder XRD was also used to characterise a sample of thermally activated LDH (the product obtained from the thermal activation). The XRD pattern shown in Fig. 3 lacks the characteristic LDH peaks and contains several additional intense high angle peaks. These peaks were removed from figures in this paper due to their high intensity. The powder XRD pattern of the thermally activated Zn/Al LDH corresponds well to reference patterns of zinc and aluminium oxides as well as small amounts of gahnite ($ZnAl_2O_4$). The presence of highly intense peaks of zinc and aluminium oxide may indicate the sample has already partially decomposed into a mixed metal oxide incapable of reformation. If this is the case a lower thermal activation temperature may improve anion sorption.

Characterisation of the LDH material recovered after the sorption of iodide and iodine is important as it may help in providing an understanding of the mechanisms involved. After treatment with iodide or iodine solution a similar LDH structure is formed in both cases the significant peaks correspond well to the reference pattern for a Zn/Al LDH (00-038-0486). Furthermore, the patterns for the LDHs prepared by reformation in iodide and iodine solutions are similar showing virtually all the same peaks as shown in Fig. 2. This indicates the successful reformation of a similar LDH structure. The similarity between the iodide and iodine treated samples may also indicate the presence of similar anions and therefore a similar mechanism of sorption in both samples. Due to the similarity in their powder XRD patterns both samples correspond well to Zn/Al LDH reference pattern as well as those of aluminium oxide iodate, zinc iodate and aluminium iodate in Fig. 2. The d_{003} spacing of the samples was also investigated and found to be 8.59Å and 8.41Å for the samples treated with iodide and iodine respectively which is slightly larger than that of the original LDH material before thermal activation.

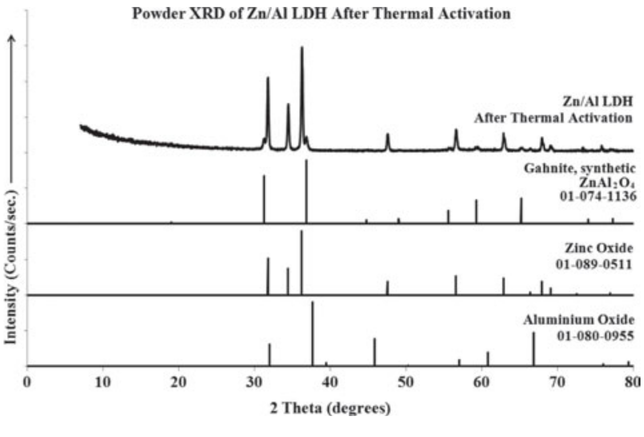

Fig. 3. Powder XRD pattern of Zn/Al LDH after thermal activation with references.

4.3. Thermal Analysis of Zn LDH

TG was carried out on a sample of the Zn/Al LDH before thermal activation with the results presented in Fig. 1. Thermal decomposition for the zinc LDH has previously been investigated by Frost et al. who proposed a mechanism of thermal decomposition of a Zn/Al LDH [27]. Four mass losses can be observed during the decomposition of the sample. The first mass loss occurs at 37°C accounting for 3.64% of the total mass loss. Due to the low temperature of this mass loss it can be attributed to the loss of weakly adsorbed water.

$$Zn_6Al_2CO_3(OH)_{16}\cdot xH_2O \rightarrow Zn_6Al_2CO_3(OH)_{16}\cdot 4H_2O + (x-4)H_2O \tag{1}$$

The second mass loss occurring at 133°C can likely be attributed to loss of interlayer water.

$$Zn_6Al_2CO_3(OH)_{16}\cdot 4H_2O \rightarrow Zn_6Al_2CO_3(OH)_{16} + 4H_2O \tag{2}$$

The third and largest mass loss occurred at 205°C accounting for 18.46% of total mass lost. Examination of the DTG curve revealed the asymmetry of the peak indicating that multiple processes are occurring simultaneously. This is not unexpected as dehydroxylation and decarbonation usually occur almost simultaneously in this temperature region. The reactions in this step proposed by Frost et al. shown below does not appear to completely match the XRD results for this sample. It is important to note that no powder XRD characterisation of samples was included the paper in which this decomposition mechanism was originally reported [27].

$$Zn_6Al_2CO_3(OH)_{16} \rightarrow Zn_6OAl_2CO_3(OH)_{14} + H_2O \tag{3}$$

$$Zn_6OAl_2CO_3(OH)_{14} \rightarrow Zn_6O_8Al_2CO_3 + 7H_2O \tag{4}$$

$$Zn_6O_8Al_2CO_3 \rightarrow (ZnO)_6Al_2O_3 + CO_2 \tag{5}$$

The reactions below better describes the decomposition of the Zn/Al LDH forming the Gahnite ($ZnAl_2O_4$) intermediary observed in the XRD pattern.

$$Zn_6Al_2CO_3(OH)_{16} \rightarrow Zn_6O_8Al_2CO_3 + 8H_2O \tag{6}$$

$$Zn_6O_8Al_2CO_3 \rightarrow ZnAl_2O_4 + 5ZnO + CO_2 \tag{7}$$

$$ZnAl_2O_4 \rightarrow Al_2O_3 + ZnO \tag{8}$$

Small features can be observed in the DTG curve at 288°C and at 605°C. It was possible to determine that the latter attributed 0.43% of the total mass lost. As the feature at 288°C cannot be adequately distinguished from the dehydroxylation/ decarbonation peak it was not possible to estimate the percentage mass lost due to this feature alone. The final significant mass loss recorded occurred at 855°C and attributed for 12.61% of total mass lost. As this temperature exceeds the region in which reformation can reliably occur this feature was not investigated further.

Assuming the formula of the Zn/Al LDH was $Zn_6Al_2CO_3(OH)_{16}\cdot 4H_2O$ the theoretical mass loss resulting from removal of interlayer water and dehydroxylation/decarbonation was calculated. The predicted loss of interlayer water was estimated at approximately 13.88% compared to 10.72% observed in that region of the TG curve (a difference of only 2.22%). The predicted mass loss resulting from dehydroxylation and decarbonation was estimated to be 36.22%, while the actual value was found to be only 18.46% (a difference of 15.31%). In both cases the observed result was lower than that of the theoretically calculated result. The discrepancy between the calculated and observed mass losses may result from impurities in the sample. Shown in XRD of the total % mass loss observed and the predicted total % mass loss reveals only a small difference between the values (7.31%). This may indicate that the decomposition of this sample did not exactly follow the mechanism proposed by Frost et al. [27].

Six mass losses could be observed in the TG curve of the LDH sample collected after thermal activation and sorption of iodide as shown in Fig. 4. The first mass loss occurred at 43°C and can be attributed to loss of weakly absorbed water. This mass loss accounted for 1.49% of the total mass loss. A large mass loss occurred at 145°C accounting for 5.89% mass loss. This mass loss is assigned to the removal of interlayer water. A third mass loss occurs at 191°C that accounts for 5.51% of total mass lost. Examination of the DTG curve reveals that two peaks overlap however they are clearly separated. This mass loss can be attributed to dehydroxylation. Three small mass losses occur at 450, 635 and 752°C. These peaks account for 1.49, 1.63 and 1.67% of total mass lost respectively.

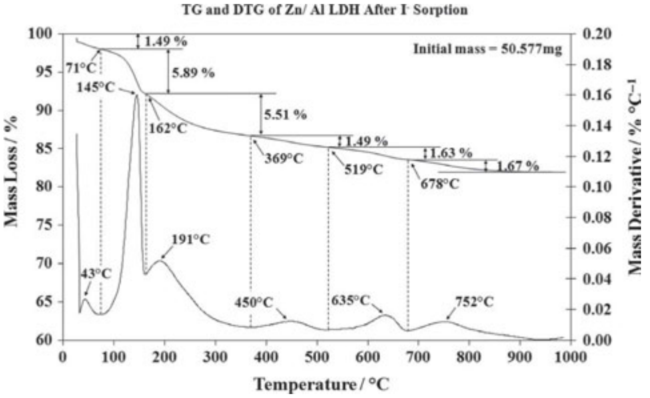

Fig. 4. TG and DTG curves of Zn/Al LDH after reformation in potassium iodide solution.

Once again calculations were performed to determine the theoretical mass loss resulting from the removal of interlayer water, dehydroxylation and removal of interlayer anions. For the purposes of these calculations it was assumed that iodide was the only interlayer anion present. The theoretical mass losses were found to be 6.89% for removal of interlayer water which compared well to the actual result of 5.89% observed. 13.78% mass loss was calculated for dehydroxylation compared to 5.51% observed. The discrepancy between the theoretical mass loss and the observed mass loss may result from partial decomposition of the sample into ZnO and Al_2O_3 during thermal activation. As ZnO and Al_2O_3 do not exhibit reformation behaviour their presence will reduce total dehydroxylation observed.

Five mass losses were observed in the TG curve of Zn/Al LDH after treatment with iodine solution shown in Fig. 5. The first occurred at 40°C and accounted for 1.93% mass loss. This peak could also be attributed to loss of weakly adsorbed water. The second mass loss was observed at 139°C accounting for 5.51% mass loss and was most likely caused by removal of interlayer water. The next mass loss occurred at 226°C and accounted for 8.38% of the total mass lost. This was the largest mass loss observed in this sample and most likely results from dehydroxylation. Another mass loss occurred at 498°C and accounted for 4.53% mass loss. The DTG curve shows two overlapping peaks that cannot be separated. The final mass loss recorded occurred at 732°C and accounted for 2.08% of total mass lost.

This TG pattern was very similar to the one observed for the TA LDH used for the removal of iodide. Theoretical mass losses were also calculated for this sample based on the assumption that the iodine is present in the form of iodide and that iodide is the only anion present in the sample. The theoretical mass loss for the removal of

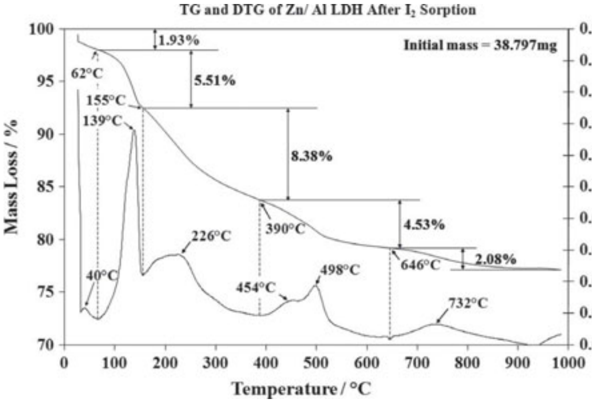

Fig. 5. TG and DTG curves of Zn/Al LDH after sorption of iodine.

interlayer water was determined to be 6.81% which compares well to the observed value of 6.89%. The theoretical mass loss of dehydroxylation was found to be 13.79% which again is greater than the observed value of 8.38%.

When the TG patterns of the LDH before thermal activation and after sorption of iodide or iodine are compared, only small changes in the temperature of dehydroxylation are observed. This can be used as a measure of the thermal stability of a LDH and indicates that the LDHs containing intercalated iodine species have similar thermal stability to those only containing carbonate in the interlayer [3].

The total mass loss for both the iodine and iodide samples were lower than that of the original Zn/Al LDH BTA (40.16%). Mass losses of 17.68% after iodide sorption and 22.43% after iodine sorption were observed. It was found that both the anion treated samples match the theoretically determined value if removal of interlayer iodide is ignored. Results are presented in Table 3 and detailed calculations of theoretical mass losses can be obtained from the supplementary materials document. This may indicate that iodine containing LDHs undergo decomposition through more complex mechanisms than those described by Frost et al. for a carbonate containing Zn/Al LDH [7]. This also provides evidence to suggest that iodine species are not removed during thermal decomposition.

Evolved gas mass spectrometry of the iodide intercalated sample shown in Fig. 6 revealed three distinct types of water corresponding to weakly adsorbed water at 34°C, interlayer water at 145°C and dehydroxylation at 206°C. Two distinct types of carbon dioxide were also observed at 213 and 424°C. Three losses of oxygen were also observed at 148, 213 and 424°C. Results suggest that almost all the mass lost above 600°C was lost as oxygen. It was also observed that no iodine containing gases measured were released during thermal decomposition

Table 3
Comparison of the observed and theoretical mass losses for all three samples analysed by TG. The theoretical mass loss of the I^- and I_2 intercalated samples was determined by combining the loss of interlayer water and dehydroxylation only. No removal of interlayer anions was included

Sample	Total observed mass loss (%)	Theoretical observed mass loss (%)	Difference (%)
BTA	42.79	50.10	–7.31
I^- Sorption	17.68	20.64	–2.96
I_2 Sorption	22.43	20.68	+1.75

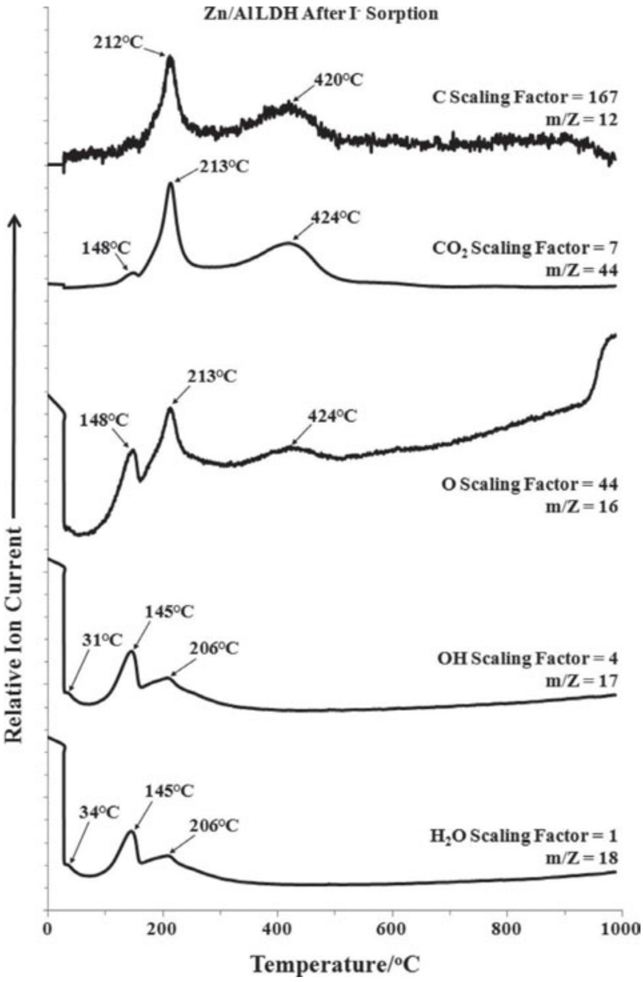

Fig. 6. Evolved gas mass spectrometry of Zn/Al LDH treated with I^- solution gases detected.

as illustrated in the ion current curves (Fig. 7). Similar results were observed in the iodine containing sample shown in Fig. 8. The most significant difference was that iodine ($m/Z = 127$) was observed between approximately 200–700°C. It is not clear why iodine is lost from this sample and not the one treated with iodide, however this may result from the presence of different (and less stable) iodine containing anions in the interlayer or simply the greater number present as the LDH was found to have a higher affinity for iodine. Two distinct features can be observed at 295 and 519°C. Losses of water occurred at 47, 143 and 212°C. Two distinct forms of carbon dioxide were also observed at 224 and 443°C. Oxygen was also detected at 145, 224, 519 and above 600°C. A small additional peak was observed in the ion current curves of water, carbon dioxide, oxygen and hydroxide at 176–177°C.

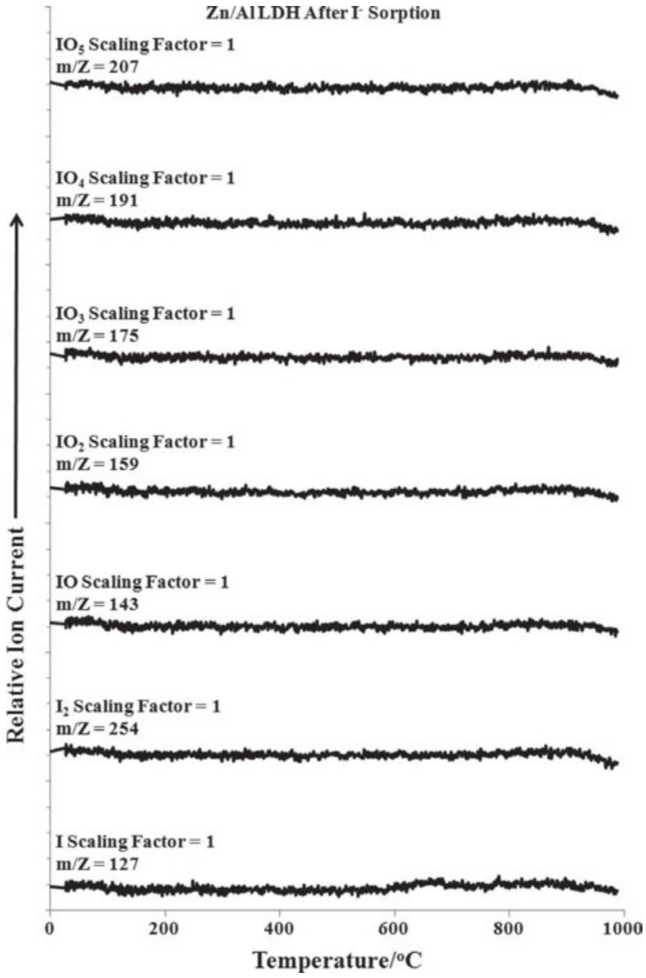

Fig. 7. Evolved gas mass spectrometry of Zn/Al LDH treated with I^- solution gases absent.

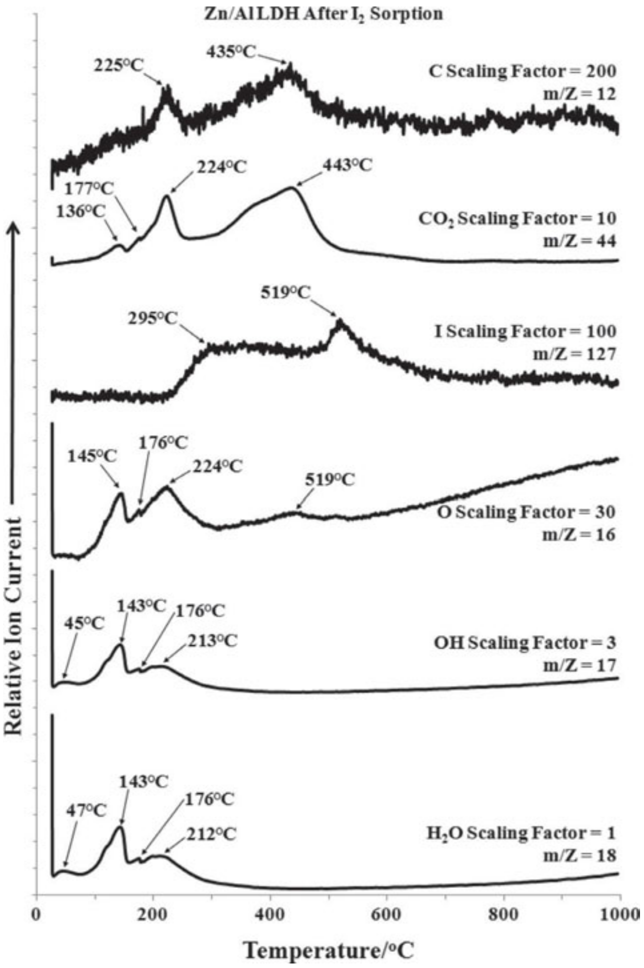

Fig. 8. Evolved gas mass spectrometry of Zn/Al LDH treated with I_2 solution.

5. Conclusions

Zinc aluminium layered double hydroxides show promise as potential sorbents for the removal of harmful iodine species from water even with relatively short mixing times and without any significant attempts to reduce sorption of carbonate (competing anion which LDHs are known to have a strong affinity for). It was found that Zn/Al LDHs were more efficient at removing iodine from (prepared by the reaction of potassium iodate and potassium iodide under acidic conditions) solution removing an estimated 99.5% of iodine in solution compared to only 36.8% removal of iodide.

Powder XRD revealed the destruction of a LDH structure after thermal activation and the successful reformation of structures similar to the original material after sorption of both iodine and iodide. The LDH may have been partially decomposed to a mixed metal oxide during thermal activation. This would reduce the efficiency of anion removal with a lower thermal activation temperature possibly providing better results. Powder XRD patterns samples recovered after treatment with iodide or iodine solutions corresponded well to the reference (00-038-0486) for a Zn/Al LDH as well as those of aluminium oxide iodate, zinc iodate and aluminium iodate. The d$_{003}$ spacing was observed to increase in both cases (8.59 and 8.41Å for the iodide and iodine treated samples respectively). The change in the d$_{003}$ spacing suggests that intercalation of different anions has occurred. Similarity of the XRD patterns may indicate the successful reformation of a similar structure to that of the original Zn/Al LDH. The similarity between the iodide and iodine treated samples may also indicate a similar composition of anions in the interlayer and therefore a similar mechanism of sorption in both samples.

Thermal decomposition of all samples appeared to be similar. A new decomposition mechanism similar to the one described in the literature was proposed for the thermal decomposition of Zn/Al LDH. A significant difference observed was that the total mass loss of samples after treatment with iodine (22.43%) and iodide (17.68%) was significantly lower than that of the original LDH (42.79%). This may indicate that iodine species form non-removable anions when intercalated into the LDH structure. If this was the case the efficiency of anion removal of the LDH would be significantly decreased after each subsequent thermal activation and reformation of the same sample. An anion-exchange step using a removable anion in solution (such as carbonate) may be necessary to make the Zn/Al LDH reusable. However, this effect may be advantageous for the long-term storage of radioactive iodine in LDH materials especially after their decomposition to mixed metal oxides at high temperatures (in excess of 1000°C) which should inhibit the reformation and anion exchange properties [2,3]. Comparison of the theoretical and observed mass losses were performed which appeared to confirm the hypothesis that iodine containing anions were not removed during thermal decomposition.

Evolved gas mass spectrometry failed to detect any iodine species lost as gases during the decomposition of iodide treated LDH sample. Iodine in its elemental form ($m/Z = 127$) was however observed to be lost at temperatures between approximately 200–700°C. The scaling factor of the plot in Fig. 8 suggests only a small quantity is observed when compared to the result of water. The loss of iodine may be due to the presence of different iodine containing anions in the interlayer or simply the greater number present as the LDH was found to have a higher affinity for iodine.

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