



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.

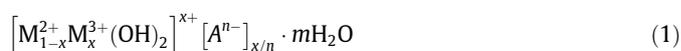
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1. Introduction

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

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