



Research paper

On the role of ultrasound and mechanical stirring for iodide adsorption by calcined layered double hydroxides



L. Iglesias^{a,b}, M.G. Álvarez^{a,b}, R.J. Chimentão^{a,b}, J.L. Leganés^c, F. Medina^{a,b,*}

^a Departament d'Enginyeria Química, University Rovira i Virgili, 43007, Tarragona, Spain

^b EMaS – Centro de Investigación en Ingeniería de Materiales y micro/nano Sistemas, 43007, Tarragona, Spain

^c Empresa Nacional de Residuos Radioactivos (ENRESA), 28043 Madrid, Spain

ARTICLE INFO

Article history:

Received 31 May 2013

Received in revised form 20 January 2014

Accepted 5 February 2014

Available online 5 March 2014

Keywords:

Iodide

Adsorption

Hydrotalcite

Ultrasound

Mixed oxides

Mass transfer

ABSTRACT

Improving the adsorption of long-term radioactive species in the underground disposal of waste waters from nuclear reactors is a key issue. The natural metal oxides or hydroxides underground have the low retention ability of anionic species. Here, calcined Mg/Al LDHs were used as adsorbents. The influence on the adsorption capacity of different intercalated guest anions (carbonate (CO_3^{2-}) and nitrate (NO_3^-)) in the parent LDH was investigated, along with the effect of ultrasonication. Two Mg/Al molar ratios (3/1 and 2/1) were compared. Adsorption capacity was strongly affected by material textural properties, and the carbonate LDH-derived mixed oxides showed the largest adsorption capacity. Mixed oxides with an Mg/Al molar ratio equal to 3 presented higher iodide adsorption due to their lower charge density. The adsorption assisted by ultrasound increased iodide removal efficiency by reducing internal diffusion limitation. Two models were used to determine adsorption capacity: Langmuir and Freundlich. The iodide adsorption was best fitted by the Langmuir equilibrium model.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Iodine-131 is one of the mobile fission gases produced in nuclear reactors. It is released from the fuel matrix as iodide (I^-) or iodine (I_2) gas to aqueous solutions (Johnson et al., 2012), generating significant amounts of radioactive waste (high-level radioactivity waste, HLRW) through the formation of ^{129}I . ^{129}I is considered to be a very hazardous radionuclide (Kauphold et al., 2007; Oscarson et al., 1986) due to its long half-life ($1.57 \cdot 10^7$ yr), the low interaction that it presents with most geological materials and its biological relevance. In aqueous media, iodine is mainly presented as iodide (I^-) and iodate (IO_3^-), depending on the pH and redox conditions (Whitehead, 1984). Under reducing conditions or in waters with a low oxygen concentration (conditions typical of groundwater), iodine exists as I^- at most pH values (Nagata et al., 2009). Several studies have therefore focused on iodide capture through sorption with different materials capable of retaining it while fulfilling other requirements such as thermal and chemical stability.

Numerous materials including geological materials like metal oxides and hydroxides, and sand and clays have been tested for their ability to remove iodide from aqueous media (Sinha et al., 1997). These materials have shown low retention of anionic species (Toraishi et al., 2002).

However, anionic clays are supposed to be good candidates for iodide capture due to their well-known anion exchange properties and capacity for reconstruction (Cavani et al., 1991; Goh et al., 2008; Palmer and Frost, 2010; Phillips and Vandeperre, 2011).

Layered double hydroxides (LDHs) are anionic clays of this type. They have positively charged brucite-type layers that can be tuned by varying not only the identity and relative proportions of the di- and trivalent cations forming the sheets but also the identity of the interlayer anions. Their general formula is represented as $[(\text{M}_1^{2+}_x \text{M}_2^{3+}_{3-x}) \cdot (\text{OH})_2]^{x+} (\text{A}^{n-})^{x/n} \cdot m\text{H}_2\text{O}$, where M^{2+} and M^{3+} are di and trivalent metals respectively, x is equal to the ratio of $\text{M}^{3+}/(\text{M}^{2+} + \text{M}^{3+})$ and A is an anion that compensates the positive charge of the metal hydroxide layer (Cavani et al., 1991).

LDH materials have been widely studied in a large number of practical applications over the last decade. As adsorbents, they are characterized by a high anion exchange capacity (comparable to that shown by exchange resins) (Cavani et al., 1991), a large surface area and a flexible interlayer space, which enable them to entrap different organic and inorganic anions (Duan and Evans, 2006).

The adsorption properties of layered double hydroxides depend on their layer charge density (MII/MIII molar ratio), guest anions and structure (i.e. uncalcined or calcined LDHs). LDHs can uptake anion species via three different mechanisms: surface adsorption, anionic exchange and reconstruction of calcined LDHs (Duan and Evans, 2006). The latter would presumably raise the uptake values compared to surface adsorption or anionic exchange. Numerous studies have reported that

* Corresponding author at: Departament d'Enginyeria Química, University Rovira i Virgili, 43007, Tarragona, Spain.

E-mail address: francesc.medina@urv.cat (F. Medina).

adsorption by calcined LDHs is considerably higher than adsorption by uncalcined LDHs (Goh et al., 2008; Parker et al., 1995). There are several reasons for this: i) increased surface area; ii) increased pore volume; and most especially iii) their reconstruction ability. LDHs have a so-called “memory effect”, whereby an LDH material can be thermally decomposed and then rehydrated in an aqueous solution to return to its original structure (Cavani et al., 1991; Erickson et al., 2005; Pesic et al., 1992). Rehydrating the calcined product regenerates the LDH, where water is absorbed to reform the hydroxyl layers, as well as adsorbing it into the interlayer along with the anion in solution. This effect has been used successfully to remove both organic and inorganic harmful anions from wastewater solutions (Lv et al., 2006a,b; Orthman et al., 2003; Palmer and Frost, 2010; Parker et al., 1995; Ren et al., 2002; Ulibarri et al., 2001). In addition, this property makes it possible to recycle and reuse the adsorbent by means of different decomposition–reconstruction cycles.

Both as-synthesized and calcined LDHs have been reported as sorbents for the decontamination of radioactive wastewater. Toraiishi et al. (2002) showed the adsorption behavior of IO_3^- in radioactive wastewater when using uncalcined LDHs with interlayer carbonate or nitrate anions. It was found that the adsorption equilibrium was reached more quickly for LDH- CO_3 than for LD- NO_3 . Calcined LDHs have also been studied as a useful resource for the nuclear industry to concentrate radioactive iodine isotopes diluted in a nuclear power plant's effluents (Lv et al., 2006a; Suárez et al., 1996).

The properties of adsorbent materials can also be modulated by means of ultrasound. Ultrasonication has been reported as improving the synthesis of adsorbent material (Climent et al., 2004; Li et al., 2013; Seida et al., 2002) as well as having exfoliation capacity (Kehal et al., 2010), which may facilitate the entry of anions into the interlayer space and thereby enhance uptake capacity. Adsorption with ultrasound (sonosorption) is considered an effective tool for removing different pollutants from waters, e.g. phenol and dyes (Vajnhandl and Le Macheral, 2007). The presence of ultrasound may increase the mass transfer rate by reducing diffusion resistance, and hence the diffusion of the iodide anions between layers should be enhanced (Frederick, 1965).

In this paper we carry out a comparative study of the adsorption of iodide by Mg/Al calcined LDHs with different Mg/Al molar ratios (2/1 and 3/1) and two different interlayer anions (carbonate and nitrate). The interlayer anion of the parent LDHs has an effect on the textural properties of their corresponding mixed oxides (Cossi and Marchese, 2010), which may in turn have an effect on the uptake capacity of the adsorbent material. We also explore how ultrasonication affects the adsorption process in contrast to mechanical stirring.

2. Experimental

2.1. Synthesis of layered double hydroxides

Nitrated and carbonated LDHs with Mg/Al molar ratios of 2 and 3 were synthesized using the co-precipitation method as follows: an aqueous solution (100 mL) containing the appropriate amount of magnesium nitrate (20–30 mmol) and aluminum nitrate (10 mmol) (Sigma Aldrich 98% and Fluka 98% respectively) was added dropwise into a beaker containing 100 mL of deionized and decarbonated water with vigorous stirring at room temperature. The pH of the solution was kept constant at $\text{pH} = 10.0 \pm 0.2$ by adding a 2 M NaOH (Sigma Aldrich 98%) solution (for nitrated HT) or a 2 M NaOH and Na_2CO_3 (Sigma Aldrich 99%) 0.05 M solution (for carbonated HT). The resulting mixture was aged under stirring overnight, then filtered and thoroughly washed with deionized water and dried at 373 K for 12 h. The preparation and aging of the nitrated HT were performed under Ar flow. The obtained solids were denoted as 21C-as and 31C-as (for carbonated HT) or 21N-as and 31N-as (for nitrated HT). Finally, the HTs were calcined for 5 h in static air at 723 K to produce mixed oxides, which

were labeled as 21X-c, where X represents the anion of the parent HT (C for carbonate and N for nitrate).

2.2. Characterization

The XRD analysis of the materials was recorded by a Siemens D5000 diffractometer with Bragg–Brentano geometry using nickel-filtered Cu $K\alpha$ radiation ($\lambda = 0.1541$ nm). The diffractograms were collected in the 2θ range of $5\text{--}70^\circ$ with an angular step of 0.05° at 3 s per step.

The textural properties of all the synthesized samples were measured by N_2 -physisorption at 77 K using a Quadrasorb SI surface analyzer. All the samples were degassed in vacuum at 393 K for 15 h prior to analysis. The BET specific surface area was calculated from the range $p/p_0 = 0.05\text{--}0.35$ in the adsorption branch, while BJH pore size distribution was calculated from the desorption branch.

Environmental scanning electron microscopy (ESEM) was carried out on the samples using a FEI Quanta 600 microscope with INCA microanalysis from Oxford Instruments operating at high vacuum with an accelerating voltage of 20 kV and a working distance of 6.6 mm. The samples were previously metalized with gold for 180 s.

Transmission electron microscopy (TEM) was performed in a JEOL 1011 apparatus using 100 kV accelerating voltage. The samples were dispersed in ethanol and then deposited on a standard 3 mm holey carbon-coated copper grid.

2.3. Iodide adsorption experiments

Adsorption tests were performed with the calcined samples. Batch experiments were carried out in 40 mL polypropylene tubes using 35 mL of potassium iodide (Sigma Aldrich 99%) solutions with concentrations ranging from 100 to 3000 ppm and 0.160 g of calcined LDH. The mixture was magnetically stirred (1000 rpm) at a controlled temperature (298 K) for 25 h. Previous experiments had shown that this is enough time to reach equilibrium. After 25 h the adsorbent was separated from the solution by centrifugation and the liquid phase was analyzed using a selective iodide electrode. All assays were carried out in triplicate and the results shown correspond to the mean values. The resultant adsorption data were fitted to Langmuir and Freundlich equations. For comparative purposes, the iodide adsorption was also performed with 21N-c and 31N-c samples while applying ultrasound treatment. The batch experiments were carried out in an ultrasonic bath at a frequency of 50 kHz. The mixture was submitted to ultrasonication for 1 h and then magnetically stirred (1000 rpm) at a controlled temperature (298 K) to complete 25 h. The procedure was applied in accordance with results obtained in previous experiments. The HT samples after iodide adsorption experiments were also characterized and are labeled as 21C-I, 21N-I, 21N-IUS (with ultrasonication), 31C-I, 31N-I and 31N-IUS, respectively.

3. Results and discussion

3.1. Effect of the molar ratio and interlayer anion of the parent LDH

The effect of the Mg/Al molar ratio on the removal of the iodide anions as well as the interlayer anion of the parent LDH was investigated. A clear influence of the Mg/Al molar ratio on the uptake capacity of the adsorbent (Table 1) was observed. Thus those materials with an Mg/Al molar ratio equal to 3 (31C-c and 31N-c) presented the highest iodide adsorption (392 and 266 $\text{mg l}^{-1}/\text{g}$ respectively). The higher adsorption capacity of these samples is due to their lower layer charge density and is in agreement with previous studies on adsorption with LDHs (Lian and Li, 2007; Palmer and Frost, 2010). Mixed oxides with an Mg/Al molar ratio of 3 also undergo the fastest reconstruction process due to the structural ordering of their cations (Pfeiffer et al., 2010), which may help the adsorption process. However, it is important to note that carbonate derived mixed oxides presented higher adsorption

Download English Version:

<https://daneshyari.com/en/article/1694687>

Download Persian Version:

<https://daneshyari.com/article/1694687>

[Daneshyari.com](https://daneshyari.com)