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Treatment and resource recovery from inorganic fluoride-containing waste produced by the pesticide industry

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ABSTRACT

The rapid development of the fluorinated pesticide industry has produced a large amount of fluorine-containing hazardous waste, especially inorganic fluoride-containing waste (IFCW). A two-step process, including extraction and recovery, was developed to recover fluorine as synthetic cryolite from IFCW produced by the pesticide industry. The optimum conditions for extraction were found to be a temperature of 75°C, an initial pH (pH_i) of 12, a 4-hr incubation time and a liquid-to-solid ratio of 40 mL/g; these conditions resulted in a fluorine extraction ratio of 99.0%. The effects of pH and the F/Al molar ratio on fluorine recovery and the compositional, mineralogical and morphological characteristics of the cryolite products were investigated. Field-emission scanning electron microscopy of recovered precipitates showed changes in morphology with the F/Al molar ratio. Coupling Fourier transform and infrared spectroscopy, X-ray diffraction indicated that the formation of AlF_6^{3-} was restricted as increasing pH. Both the amount of fluorine recovered and the quality of the cryolite were optimized at initial pH = 3 and a F/Al molar ratio 5.75. This study proposed a reliable and environmentally friendly method for the treatment of fluoride-containing wastes, which could be suitable for industrial applications.

Introduction

In agriculture, fluorinated pesticides have attracted much attention for their ability to control a wide range of pests and have been increasingly used in place of organochlorine and organophosphorus insecticides (Hadfield et al., 1992; Leroux et al., 2008). In the last decade, newly developed fluorinated pesticides, such as cyhalothrin, fenfluthrin, and tefluthrin, accounted for 30%–50% of the total amount of pesticide used (Manteau et al., 2010). The production of fluorinated pesticides generates a large amount of fluorinated waste, which contains fluorine-related inorganic and organic compounds. Improper disposal of such waste could cause fluoride contamination of ground water, bodies of water and soil and thus endanger public health (Ayoob and Gupta, 2006; Amini et al., 2008; Ozsvath, 2009).

The most commonly used treatment technologies for fluorine-containing waste include physical separation, thermal treatment, solidification/stabilization and chemical extraction (Pulvirenti et al., 1996; Pong et al., 2000; Wang et al.,

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2012). Among these, chemical extraction can be performed at low temperature and pressure, thereby reducing the need for additional landfill space and conserving natural resources (Iranpour et al., 1999; Vegliò et al., 2003). In addition, soluble fluorine can be recovered, thereby utilizing resources more efficiently. Wang et al. (2013) used a solution of aluminum salt as the fluorine coordination reagent to scrub fluoride from the loaded organic phase of bastnaesite, and the resultant scrubbing solution that contained aluminum fluoride complexes produced cryolite (Na_3AlF_6). Lisbona et al. (2013) reported that a two-step extraction process that included water leaching and $AlF_2OH{\cdot}1.4H_2O$ precipitation with a mixture of $Al(NO_3)_3{\cdot}9H_2O$ and HNO_3 could extract more than 92% of the fluorine from spent pot lining, and the selective precipitate, $AlF_2OH{\cdot}1.4H_2O$, was transformed into smelter grade AlF_3.

Inorganic fluoride-containing waste (IFCW) from the pesticide industry is usually disposed of in hazardous waste landfills after solidification and stabilization. However, to reduce the leaching toxicity of the highly soluble fluoride, a significant amount of reagents such as lime or cement is required, thus wasting precious landfill volume. To the best of our knowledge, application of chemical extraction and resource recovery to IFCW from pesticide industries has rarely been reported. It is imperative to develop an environmentally friendly process for IFCW treatment that is characterized by low cost, reduced secondary pollution and generation of high-value by-products.

For IFCW that primarily contains dissoluble salt (NaF), leaching can be applied as part of the fluorine recovery process (Aghaie and Samaie, 2006). However, the pH value has an important influence on the dissolution of NaF. A relatively high concentration of alkali (*e.g.*, 12 g/L of F^- in 30–50 g/L NaOH solution) can decrease the fluoride solubility (Morales et al., 2007), and for the system NaF–NaX–NaOH (X = ClO_4, PO_4, SO_4 and NO_3), the fluoride solubility varies with the concentration of NaOH (Weber et al., 2000). Furthermore, water-soluble organic matter and metal ions, such as Ca^{2+} and Al^{3+}, can affect the efficiency of fluorine extraction in solutions with different pH values (Lisbona and Steel, 2008; Wang et al., 2012).

Generally, the fluorine products that are recovered from IFCW or wastewater include NaF (Jagtap et al., 2012), CaF_2 (Aldaco et al., 2007), Na_3AlF_6 (Grobelny, 1976), AlF_3, and $AlF_2(OH)$ (Lisbona et al., 2013), among other compounds (Miksa et al., 2003; Aldaco et al., 2005). NaF and CaF_2 have relatively low economic value. Furthermore, the requirements for the raw materials and production process for AlF_3 and $AlF_2(OH)$ are rigorous (Lisbona and Steel, 2008). In comparison, Na_3AlF_6 is much less expensive and has become almost indispensable in certain branches of the chemical industry, *e.g.*, as an ingredient for wear-resistant material, as a whitener for enamel, as an opacifier for glass (Halland, 1911), and most importantly, as flux in the smelting of aluminum (the Hall-Héroult process) (Haupin, 1983). In addition, because of its molecular formula, the precipitation process of Na_3AlF_6 consumes a minimum amount of aluminum, thereby leading to both economic and environmental benefits.

Therefore, the aims of our study were (1) to develop a facile and low-cost process for treating IFCW, including fluorine extraction and recovery; (2) to investigate the effects of temperature, time and initial pH (pH_i) on fluorine extraction from IFCW; (3) to investigate the reaction mechanisms of fluorine recovery in the form of Na_3AlF_6 at different F/Al molar ratios and pH_i values; and (4) to assess the feasibility of using the fluorine recovery and extraction process in industrial applications.

1. Materials and methods

1.1. Materials

All chemicals were analytical-reagent grade and purchased from Sinopharm Chemical Reagent Co., Ltd., China. IFCW was collected from a hazardous waste treatment and disposal facility, and was generated by Jiangsu Yangnong Chemical Group Co., Ltd. which is the largest producer of pyrethroids in China. After saponification of fluorine-containing intermediates, the reaction solution was cooled for crystallization and filtered, IFCW was then obtained. After being dried at 105°C for 24 hr, the IFCW was sieved through 150-μm meshes for further experiments. The elemental composition of the IFCW was determined using an X-ray fluorescence spectrometer (XRF, XRF-1800, Shimadzu, Kyoto, Japan) and an elemental analyzer (EA3000, Eurovector, Redavalle, Italy), as following: Na 49.60%, F 39.52%, Cl 4.23%, C 2.31%, N 0.46%, Ca 0.32 mg/g, P 0.28 mg/g, Cr 0.22 mg/g, Al 1.09 mg/g, and Fe 0.58 mg/g. The X-ray diffraction (XRD, D8 advance, Bruker, Billerica, Germany) pattern of IFCW was dominated by the peaks that are associated with NaCl and NaF, as shown in Fig. 1. The results demonstrated that the organic matter content in the IFCW was quite low and that the fluorine was in the form of NaF. Considering the strong leachability and high content of NaF, the waste was not suitable for solidification/stabilization which required a great amount of precipitant. Therefore the removal of NaF meanwhile with resource recovery was adopted.

1.2. Extraction experiments

Batch experiments were conducted in duplicate in a shaking incubator (SPX-250B-D, Boxun, Jiangsu, China) maintained at 150 r/min using a 250-mL polyethylene jar. For the kinetics investigations, 5.0 g of IFCW and 200 mL of deionized water

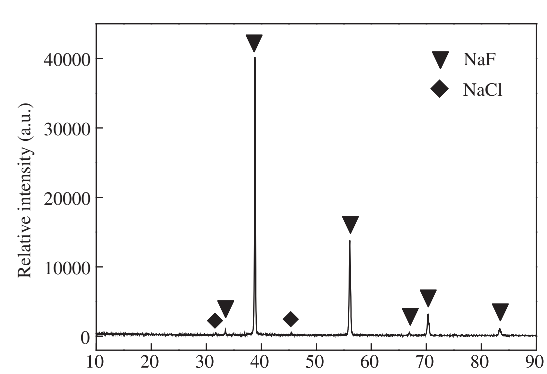

Fig. 1 – X-ray diffraction (XRD) pattern of inorganic fluoride-containing waste (IFCW).