Applied Clay Science 114 (2015) 190–196

Contents lists available at ScienceDirect

Applied Clay Science

journal homepage: www.elsevier.com/locate/clay

Research paper

A comparative study of tubular halloysite and platy kaolinite as carriers for the loading and release of the herbicide amitrole

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ARTICLE INFO

Article history:
Received 1 April 2015
Received in revised form 10 May 2015
Accepted 29 May 2015
Available online 14 June 2015

Keywords:
Clay minerals
Methoxy modification
Intercalation
High-capacity loading
Controlled release

ABSTRACT

Nanosized tubular halloysite (Hal) and platy kaolinite (Kaol) were used as carriers for the loading and release of the herbicide amitrole (AMT). The AMT loading content in Hal was 17.5 mass% (69.9% greater than in Kaol). This result is attributed to the significant loading of AMT in the lumen of Hal. The methoxy modification of Hal and Kaol made their interlayer spaces available for the intercalation of AMT, which substantially promoted the AMT loading. The AMT loading content in methoxy-modified Hal was 30.5 mass%, corresponding to 27.9% intercalated AMT and 72.1% non-intercalated AMT. The AMT loading content in methoxy-modified Kaol was 20.8 mass%, corresponding to 47.6% intercalated AMT and 52.4% non-intercalated AMT. The release profiles of the AMT fit with the modified Korsmeyer–Peppas model. The methoxy-modified Kaol exhibited a slow release of AMT, which resulted from two factors: (i) the high proportion of intercalated AMT, the diffusion of which was restricted by the lamellar structure of the methoxy-modified Kaol, and (ii) the long diffusion path of intercalated AMT because of the large size of Kaol particles in comparison with Hal particles.

1. Introduction

Pesticides, mainly insecticides, herbicides, and fungicides, are used worldwide to increase global agricultural productivity, to reduce insect-borne endemic diseases, and to protect plantations (Ecobichon, 2001). However, the excessive use of pesticide has created serious health problems, such as birth defects, neurobehavioral disorders, and cancer (Rothlein et al., 2006; Nasterlack, 2007). Environmental contaminations are also a concern, such as air, water, and soil pollution, bioaccumulation and biomagnification, pest resistance and resurgence, and loss of biodiversity and ecosystem resilience (Yuan et al., 2010; Atreya et al., 2011). There has been a great interest in developing controlled-release formulations of pesticides because such formulations are able to provide safer conditions of use and minimize the potential environmental contaminants by simultaneously reducing the amount of pesticide used and increasing its efficiency (Nennemann et al., 2001). A series of synthetic and natural materials have been proposed as carriers for pesticide retention and release. These carriers include synthetic polymers, such as poly(vinyl alcohol) (Hartmann et al., 1985; Alemzadeh and Vossoughi, 2002), polylactic acid (Taki et al., 2001), and poly(hydroxybutyrate) (Grillo et al., 2011), and some natural organic compounds, such as starch (Cao et al., 2005), ethylcellulose (Sopena et al., 2005), alginate (Isiklan, 2006), and chitosan (Yi et al., 2011).

In addition, natural porous materials that can be used as pesticide carriers in controlled-release formulations, such as zeolite (Zhang et al., 2006) and some swelling clay minerals, e.g., montmorillonite (Celis et al., 1999, 2002; Carrizosa et al., 2000; Hermosin et al., 2001, 2006; Undabeytia et al., 2013) and hydrotalcite (Celis et al., 1999; Bruna et al., 2008), have attracted considerable attention. Natural zeolites and clay minerals have several advantages for use as pesticide carriers: (i) in comparison with synthetic porous materials, these natural minerals are readily available at low cost because of their abundant deposits; (ii) they are environmentally friendly because they are common soil constituents; and (iii) the loading of pesticides on these carriers is readily achieved *via* simple adsorption and/or ion exchange because they normally possess high ion-exchange capacity. Some ionic pesticides, such as imazamox (Celis et al., 1999), glyphosate (Zhang et al., 2004), and paraquat (Zhang et al., 2006), investigated in related studies with zeolites and clay minerals used as carriers, have exhibited excellent loading and controlled-release behavior. However, much less effort has been paid to the investigation of the loading of nonionic pesticides on zeolite and clay minerals because such pesticides cannot be loaded *via* ion exchange. Celis et al. (2002) have found that Wyoming montmorillonite (CEC: 76 mmol/100 g) has a low loading of the nonionic pesticide hexazinone (approximately 0.6 mass%), and Arizona

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http://dx.doi.org/10.1016/j.clay.2015.05.024
0169-1317/

montmorillonite (CEC: 120 mmol/100 g) has a negligible loading of hexazinone. These low levels are because the neutral pesticide molecule is hard to be adsorbed on the highly charged surface of montmorillonite.

Amitrole (3-amino-1,2,4-trizole; AMT) is a non-selective polar herbicide with a wide spectrum of activity against annual and perennial broadleaf and grass-type weeds, acting *via* inhibition of carotenoid biosynthesis (Oesterreich et al, 1999). It is of low toxicity to mammals. Owing to its high efficacy in weed control, it is widely used on fallow land prior to sowing, along roadsides and railways, and on wasteland. Because of its high mobility, high water solubility (280 g/L, 25 °C), and low volatility (Fontecha-Camara et al., 2008), AMT is readily dissolved in soil solution and is a potential pollution source for the ground water and surface water through leaching, and then contaminate food through plants, fruits, and water media (Oesterreich et al, 1999). The development of controlled-release formulations for highly soluble herbicides like AMT is therefore a big requirement, however, some challenges still exist, e.g., high-capacity loading of herbicides is difficult to achieve in agrochemical industry. Hartmann et al. (1985) have found a controlled-release formulation of AMT, which was prepared by firstly converting AMT into N-phosphorylated AMT *via* acylation with phenyl- and 4-nitrophenyl phosphorodichloridate and then attaching the resultant to poly(vinyl alcohol) *via* esterification. AMT in the obtained product, with a loading content of approximately 20 mass%, exhibited a slow release from poly(vinyl alcohol). However, the preparation of this controlled-release formulation was somewhat complicated. Although swelling clay minerals, such as montmorillonite, have been widely used as carriers for herbicides, they seem not to be ideal carriers for the controlled release of AMT. The reason is that AMT has a p*K*a value of 4.1 and is not charged in a wide range of pH, so it is difficult to load AMT on montmorillonite through ion exchange. Morillo et al. (1991) have used Na^+-, Li^+-, Mg^{2+}-, and Zn^{2+}-saturated montmorillonites as hosts to adsorb AMT and have found that AMT was primarily adsorbed on these montmorillonites as neutral molecules and exhibited a low level of loading (approximately 1.5 mass%).

Kaolinite (Kaol) is a 1:1 clay mineral consisting of $AlO_2(OH)_4$ octahedral sheet and SiO_4 tetrahedral sheet. The adjacent sheets are connected together by apical oxygen of tetrahedral SiO_4 sheet to form a Kaol layer with the ideal chemical formula $Al_2Si_2O_5(OH)_4$. The Kaol layers are linked by hydrogen bonding. The mismatch between the smaller octahedral sheet and the larger tetrahedral sheet is corrected *via* the rotation and distortion of the tetrahedral sheet to form a platy morphology. Kaol particles are normally of the micro-scale in sizes (Castellano et al., 2010). Conventionally, Kaol is often applied as ceramic raw material, as filler in clay polymer nanocomposite, as filler and coating in paper, and as active pharmaceutical ingredient and excipient in pharmaceutics (Prasad et al., 1991; Murray, 2000; Conceição et al., 2005; Carretero and Pozo, 2009, 2010), but is rarely used as a carrier because of its low cation exchange capacity (CEC less than 10 mmol/100 g) (Ma and Eggleton, 1999) and its low specific surface area (*SSA* between 10 and 20 m^2/g) (Castellano et al., 2010). When Kaol was used as carrier, the guest molecules (e.g., salicylic acid, ibuprofen) only adsorbed on the external surface of Kaol (Bonina et al, 2007; Mallick et al., 2008), could not be directly intercalated into the hydrogen-bonded interlayer. The previous studies have proved that the development of the interlayer space of Kaol as additional loading space for guest molecules (e.g., 5-fluorouracil, AMT) could be achieved by methoxy-modification (Tan et al., 2014a, 2015). This further intercalation is ascribed to that the methoxy-modification introduced a plane of methoxy groups into the interlayer space of Kaol weakening the original hydrogen bonding between adjacent layers. Therefore, the carrier-performance of Kaol was significantly promoted by methoxy-modification (Tan et al., 2014a, 2015).

Halloysite (Hal), a polymorph of Kaol, has similar chemical constitution and crystal structure to Kaol, but has different microstructure and morphology. Compared to Kaol, Hal has an additional monolayer of water molecules between the unit layers. As a result, Hal accommodates the mismatch between the octahedral sheet and tetrahedral sheet *via* the wrapping of layers to form a nanosized tubular morphology (Singh, 1996). Generally, tubular Hal varies in length from submicrons to several microns, occasionally even reaching lengths of >30 μm (Joussein et al., 2005), and it ranges in external diameter from approximately 30 to 190 nm and in internal diameter from approximately 10 to 100 nm (Yuan et al., 2008, 2013). These sizes vary in different Hal deposits (Pasbakhsh et al., 2013). The unique mesoporous (2–50 nm) or even macroporous (>50 nm) lumen of Hal makes it a promising carrier for loading and controlled release of various guests (Price et al., 2001; Levis and Deasy, 2003; Veerabadran et al., 2007, 2009; Lvov et al., 2008; Abdullayev and Lvov, 2011; Yuan et al., 2012; Tan et al., 2013, 2014b). Yuan et al. (2012) has proposed that the micromorphology of Hal exerted substantial influence on its loading capacity that Hal with high *SSA* exhibited a large loading content of Orange II. Based on this study, it can be postulated that the carrier-performance of tubular Hal and platy Kaol may exhibit huge difference because of the significant discrepancy in microstructure and morphology.

In this work, Hal and Kaol were used as carriers for the loading and release of AMT, and the interlayer methoxy modification was adopted to increase the loading of AMT. Attention was focused on the performance of Hal and Kaol as carriers for the loading and release of AMT and on the mechanism determining the different performances of the two types of clay minerals.

2. Experimental methods

2.1. Materials and methods

A high-purity Kaol sample, obtained from Maoming, Guangdong Province, China, was used as received without further purification. The raw Hal sample was collected from Linfen, Shanxi Province, China. The finest Hal particles were obtained by simple sedimentation and then dried overnight at 120 °C.

The methoxy-modified Hal and Kaol were prepared as follows: dimethyl sulfoxide (DMSO) was first intercalated into the interlayer space of Hal and Kaol as previously reported (Yang et al., 2012). Then, 5.0 g of the DMSO-intercalated clay mineral sample was added to 100 ml of methanol (MeOH) and stirred for 7 days. The solids in the mixture were separated *via* centrifugation and then stored in a wet state for further use. The methoxy-modified Hal and Kaol were labeled as Hal_{MeOH} and $Kaol_{MeOH}$, respectively.

The loading of AMT was achieved using soaking methods. A sample of 2.0 g of AMT (99%, purchased from Meryer) was dissolved in 20 ml of MeOH, and approximately 1.0 g of each clay mineral, before and after methoxy modification, was added under constant stirring for 24 h at room temperature. The solid part of the dispersion was separated *via* centrifugation and dried overnight at 80 °C. The AMT-loaded clay mineral samples were identified by adding the prefix "AMT-" to the starting materials; for example, AMT-Hal_{MeOH} refers to the Hal that was modified with MeOH and then loaded with AMT.

The AMT-release tests were conducted using an RCZ-8M dissolution tester (Tianjin TDTF Technology Co. Ltd., China) following a paddle method. Approximately 0.5 g of AMT-loaded clay mineral sample was sealed in a dialysis bag (molecular weight cutoff: 3500 Da), and then soaked in 500 ml of distilled water at room temperature with a rotation speed of 100 rpm. At suitable intervals, 5 ml of the dissolution medium was withdrawn, and an equivalent volume of fresh medium was added. The AMT content was determined at 239 nm using a PerkinElmer LAMBDA 850 UV/Vis spectrophotometer. Each dissolution test was performed in triplicate.

2.2. Characterization methods

The X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Advance diffractometer with a Ni filter and Cu Kα radiation (λ =