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Heptanoic acid adsorption on grafted palygorskite and its application as controlled-release corrosion inhibitor of steel

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HIGHLIGHTS

- Chemical characterizations confirmed the APTES-grafting to palygorskite fibers.
- Silanol and NH_3^+ sites of grafted-APTES can be used as tank of organic compounds.
- Heptanoate anions bound to NH_3^+ of grafted-APTES can be released in NaCl solution.
- The organo-inorgano composite constitutes a controlled-release corrosion inhibitor.

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ABSTRACT

This study deals with the anchoring of heptanoic acid (HC_7) as a corrosion inhibitor to palygorskite clay mineral originated from High Atlas of Marrakech (Morocco) beforehand grafted with 3-aminopropyltriethoxysilane (APTES) entities. Physicochemical characterizations (XRD, FTIR, TG-MS, zeta potential measurements) confirmed the success of the APTES-grafting to silanol sites of palygorskite fibers edges and the heptanoate anions bonding to terminal NH_3^+ sites of grafted-APTES. Then, full-factorial design allowed optimizing the conditions of heptanoate adsorption. Preliminary electrochemical measurements revealed that functionalized grafted palygorskite (C_7-APTES–Pal) can progressively release the heptanoate corrosion inhibitor in 0.1 M NaCl solution to inhibit the steel corrosion processes.

1. Introduction

Clay minerals have in recent years many advanced technological applications in various fields. They have been widely used in adsorption domain for the removal of heavy ions [1–3], dyes [4,5] and other organic compounds [5,6]. Also they are used in catalysis or as catalysts supports [7]. Likewise, they can act as corrosion inhibitor nanocontainers to be incorporated in protective coating of metals [8,9].

Palygorskite abbreviated as Pal, also known as attapulgite, is a microcrystalline hydrated magnesium aluminum silicate with common microfibrous morphology and a global theoretical chemical formulas of the type $(Mg,Al)_5Si_8(OH)_2(H_2O)_4$. As we described in details elsewhere [10], the structure of palygorskite, according to Bradley's model [11,12], consists of an alternation of ribbons and nanometric cavities (tunnels) that elongate in the direction of the *c*-axis as described in Fig. 1. Each structural ribbon is made up of two tetrahedral silica sheets (T) sandwiching a central octahedral sheet (O) of magnesium and aluminum oxide-hydroxide. Tetrahedral sheets are continuous via Si–O–Si bridges in which the apical oxygens are alternatively inverted pointing in opposite directions and binding to a discontinuous octahedral sheet (O). Owing to the discontinuity of the silica sheets, silanol groups (Si–OH) are present on the external surface of the silicate particles [13,14]. These sites are located at the edges of the channels (*i.e* those tunnels acceding to the external surface of the silicate) and are directly accessible to reagents such as silanes allowing to the preparation of organic–inorganic materials derived from the fibrous clay containing different surface organic functions [13].

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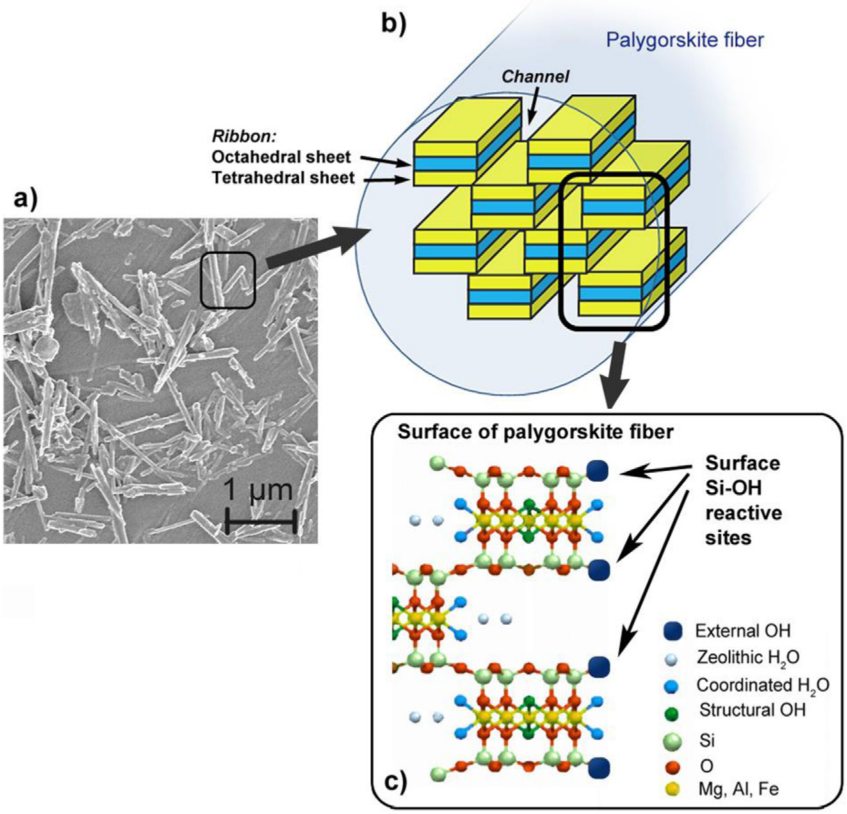

Fig. 1. Multi-scale description of the structure of palygorskite clay: (a) SEM micrograph of Na^+ exchanged purified palygorskite (Na^+–Pal), (b) Schematic overview of ribbons and channels, (c) orojection on (001) plane of the crystallographic structure showing the Si–OH reactive sites.

The dimensions of rectangular palygorskite channels are of about 3.7×6.0 $Å^2$ wide [15]. They contain two kinds of water molecules, ones (OH_2) coordinated to the edges octahedral cations and the zeolitic water (H_2O) weakly bonded to the former by hydrogen bondings. The different substitutions of octahedral and tetrahedral sites in the ribbons provoke an excess of negative charges that are compensated by the presence of exchangeable cations (Na^+, K^+, Ca^{2+}) in the nanometric channels.

The present study has the objective to use the high surface concentration of silanol groups on palygorskite fibers to form a tank of corrosion inhibitors to be used as pigments in polymeric films as paints. This strategy was also developed with other low-cost and easy-available clay as halloysite nanotubes [16]. Another strategy is the synthesis of more expensive polyelectrolyte nanocapsules [17]. In these two cases, the release of corrosion inhibitors is activated by the presence of corrosive anions as chlorides, or by local changes in pH on surfaces, in contrary to the classical release mechanism of anticorrosive pigments controlled by their solubility [18]. In a first approach, pigments are tested in corrosive solution in contact with metal surface in order to evaluate their corrosion inhibition efficiency without the polymeric film [19].

In this context, the adsorption of heptanoic acid in aqueous solution onto the High Atlas Marrakech palygorskite subsequently modified by grafting of 3-aminopropyltriethoxysilane (APTES) is studied and optimized by using experimental design in this paper. Indeed, carboxylic acid, like heptanoic acid, was reported to be an interesting nontoxic corrosion inhibitor [20,21]. The inhibitive effect of carboxylic acid is due to its functional groups (–COOH) which can form insoluble and hydrophobic metallic soaps on the metal surface. Especially, it was reported that straight chain aliphatic monocarboxylates of general formula $CH_3(CH_2)_{n-2}COONa$ with $7 \leq n \leq 11$ (noted NaC_n) have a good inhibitor property in the case of aqueous corrosion of iron [22]. The grafted palygorskite was characterized by X-ray diffraction (XRD), Fourier Transform Infra-Red Spectroscopy (FTIR), and thermogravimetric measurements coupled with mass spectroscopy (TG-MS). The surface modifications of the clay mineral were evaluated by ζ potential measurements. Then, the effect of heptanoate release on the electrochemical behavior of iron was evaluated by potentiodynamic electrochemical measurements on iron in corrosive solution containing grafted palygorskite.

2. Experimental

2.1. Palygorskite material

Palygorskite, involved here in this study, was isolated from clay picked up from Marrakech High Atlas region, Morocco and exchanged with Na^+ (labeled Na^+–Pal) according to respective purification and homoionisation procedures described in details elsewhere [23]. Characterizations performed by B. Rhouta et al. [10] showed that this palygorskite is predominantly dioctahedral, deficient in zeolitic water and associated with 5 wt.% of sepiolite. The composition of this palygorskite was found on the basis of 26 oxygens to be $(Si_{7.97}Al_{0.03})(Mg_{2.17}Al_{1.46}Fe_{0.40}Ti_{0.05})(Ca_{0.03}\text{-}Na_{0.07}K_{0,03})O_{20.18}(OH)_{1.94}(H_2O)_{3.88}$, 2.43 H_2O. Its CEC, BET specific surface area and total porous volume were assessed to be 21.2 meq 100 g^{-1}, 116 m^2 g^{-1} and 0.458 cm^3 g^{-1} respectively [24].

2.2. Preparation of grafted palygorskite

The heptanoic acid (99 wt.%), 3-aminopropyltriethoxysilane (APTES) (99 wt.%), HCl (37 wt.%) and NaCl (99 wt.%) were purchased