



## Research paper

# Intercalation of two phenolic acids in an ionic liquid–kaolinite nanohybrid material and desorption studies



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## ARTICLE INFO

## Article history:

Received 15 July 2013

Received in revised form 25 January 2014

Accepted 28 April 2014

Available online 11 June 2014

## Keywords:

Kaolinite

Nanohybrid

Intercalation

Release

Gallic Acid

Salicylic Acid

## ABSTRACT

A new ionic liquid kaolinite nanohybrid material was obtained by the grafting of 1-(2-hydroxyethyl)-pyridinium chloride (HEPC) in the mineral interlayer spaces. The XRD of the resulting material confirmed the intercalation of the ionic liquid with an interlayer expansion of 5.7 Å. Thermogravimetric analysis characterization highlighted the loss of organic matter and allowed the determination of the empirical formula of the composite:  $\text{Al}_2\text{O}_3\text{Si}_2\text{O}_2(\text{OH})_3(\text{OH}_{0.75})(\text{HEPC})_{0.25}$ . In this material, the associated anions remain free and can be replaced by other anions having a suitable size to fit into the interlayer. This was demonstrated by cyclic voltammetry after a pre-concentration step in a solution of Salicylic Acid (SA) or Gallic Acid (GA) in their anionic form. Intercalation/de-intercalation of these phenolic organic anions was then investigated. The kinetics of intercalation of these compounds was fast, with the equilibrium achieved after less than 30 min. Maximum adsorption capacity (determined by the Langmuir model) for SA (781  $\mu\text{mol/g}$ ) was close to the estimated value (867  $\mu\text{mol/g}$ ). In the case of GA (484  $\mu\text{mol/g}$ ), the smaller intercalated amount is plausibly due to the presence of GA in the form of di-anions. Desorption of these compounds performed in a 0.1 M phosphate buffer solution at pH 7 showed that SA was de-intercalated with fast kinetics (after 1 min, release was almost complete). In the case of GA, the process was slower and the equilibrium reached after about 20 min. These promising results demonstrate that the modified kaolinite may be used to store and control the release of chemical compounds, and also may be used as adsorbent for the removal of aqueous phenolic organic anions.

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## 1. Introduction

Phenolic compounds have interesting redox properties responsible for their antioxidant activity associated to their free radical scavenging properties. They are used in the food industry as natural preservatives and also in cosmetics. Some are known for their activity in the regulation of cholesterol and also for their effectiveness in protecting the human body against hypertension and cardiovascular disease (Cláudio et al., 2012; Du et al., 2009). Phenolic acids represent an important class of these compounds. They include phenolic compounds having at least one carboxylic acid function (Robbins, 2003). In recent years, research has been carried out for the synthesis of materials that can encapsulate various organic chemical compounds of biological interest in order to protect them from degradation during storage and especially during transport in the body and also to control their release once the target is reached (Duncan, 2003; Liu et al., 2008; Vivero-Escoto et al., 2010). Layered Double Hydroxides (lamellar materials with anion exchange properties) are widely used for this purpose for

anionic compounds such as phenolic acids (Khan et al., 2001, 2009; Richardson-Chong et al., 2012). However, the release control is difficult to achieve (Gunawan and Xu, 2008), mainly because of the poor selectivity of the materials.

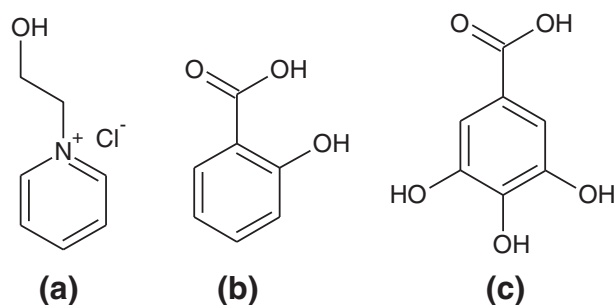
Phenolic acids are widely found in plants (wood, bark, and fruits amongst other) and are generally found in undesirable amounts in agricultural or food industries waste water. Important pollution effects are associated with these compounds through Chemical Oxygen Demand (C.O.D.) increases (Du et al., 2009; Noubigh et al., 2008). Materials having the property to accumulate efficiently these compounds may therefore be useful in environmental remediations, as they could be used as adsorbent for the treatment of industrial effluents.

Inspired by the approach used for the Layered Double Hydroxides (LDHs) (Khan et al., 2001, 2009; Richardson-Chong et al., 2012), a modified kaolinite nanohybrid material with anion exchange properties was used to study the intercalation and desorption of Salicylic Acid (SA) and Gallic Acid (GA) (structures presented in Scheme 1(b) and (c)), used here as model compounds of phenolic acids.

Kaolinite, a 1:1 clay mineral, has been so far scarcely used for the preparation of grafted organic–inorganic hybrid materials. Unlike in the case of smectites, kaolinite is not easily expandable. The main reason is the strong interactions between adjacent layers due to the presence of

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**Scheme 1.** Chemical structures of 1-(2-hydroxyethyl)-pyridinium chloride (HEPC) (a), Salicylic Acid (b) and Gallic Acid (c).

a permanent dipole in the interlayer and the abundant hydrogen bonds linking the siloxane plane to the aluminol surface (Bergaya et al., 2006). This makes the intercalation and the grafting of organic compounds on the internal surfaces of kaolinite more challenging. Several works have shown that it is possible to obtain Al–O–C covalent bonds on the kaolinite interlayer surfaces (de Faria et al., 2010; Gardolinski and Lagaly, 2005; Hirsemann et al., 2011; Komori et al., 2000; Letaief and Detellier, 2009; Tunney and Detellier, 1993). Various derivatives of kaolinite were synthesized successfully in recent years by grafting alcohols, organosilanes and especially ionic liquids on the internal surfaces (Itagaki and Kuroda, 2003; Letaief and Detellier, 2009; Tunney and Detellier, 1993). Stability tests have shown that these materials exhibit excellent resistance to hydrolysis (Letaief and Detellier, 2007). Indeed, their integrity is retained even after several weeks in water.

During the grafting of ionic liquids reported in previous papers, the cation was grafted onto the aluminol surface, leaving the counter anion free in the interlayer in order to maintain charge neutrality. The materials thus possess anion exchange properties as LDHs do, but with no swelling properties: it is the size of the grafted cation which controls the basal spacings (Dedzo et al., 2012). These materials have been successfully applied to the qualitative and quantitative electroanalysis of anions in an aqueous solution (Dedzo and Detellier, 2013; Dedzo et al., 2012; Letaief et al., 2008; Tonle et al., 2009) and for anion adsorption (Matusik and Bajda, 2013).

In this work, kaolinite was functionalized by a pyridinium-based ionic liquid. After an exhaustive characterization, the ability of this new material to accumulate between its expanded layers the anionic forms of SA and GA was studied. The release of these compounds in a phosphate buffer solution pH 7 was also investigated.

## 2. Experimental

### 2.1. Chemicals

2-Chloroethanol, Pyridine, Salicylic Acid and Gallic Acid were purchased from Aldrich. SA and GA were converted to their anionic forms using a 1 M sodium hydroxide solution and a pH-meter to monitor the pH of the solution. Throughout this study, the mentions to SA and GA were related to the anionic form of Salicylic Acid and Gallic Acid. All other chemicals (sodium hydrogenophosphate, sodium dihydrogenophosphate, dimethylsulfoxide, anhydrous ethylether and methylene dichloride) were of analytical grade.

### 2.2. Synthesis of ionic liquids

1-(2-Hydroxyethyl)-pyridinium chloride (HEPC) (Scheme 1(a)) was obtained by mixing 0.12 mol of 2-Chloroethanol and 0.1 mol of Pyridine. The mixture was then stirred at 80 °C for 48 h. The product was then fully washed with diethyl ether. The residual solvent was then evaporated in a rotary evaporator and the final solid product

stored in a tightly closed vial to avoid moisture.  $^1\text{H}$  NMR:  $\delta$  4 ppm (m, 2 H, HO-CH<sub>2</sub>-CH<sub>2</sub>-N<sup>+</sup>), 4.6 ppm (m, 2 H, HO-CH<sub>2</sub>CH<sub>2</sub>-N<sup>+</sup>), 8 ppm (m, 2 H, CH-CH-N-CH-CH), 8.5 ppm (m, 1 H, CH-CH-N-CH-CH-CH), 8.7 ppm (m, 2 H, CH-CH-N-CH-CH).  $^{13}\text{C}$  NMR:  $\delta$  60.3 ppm (1 C, HO-CH<sub>2</sub>-CH<sub>2</sub>-N<sup>+</sup>), 63.5 ppm (1 C, HO-CH<sub>2</sub>-CH<sub>2</sub>-N<sup>+</sup>), 128.2 ppm (2 C, CH-CH-N-CH-CH), 144.7 ppm (2 C, CH-CH-N-CH-CH), 146.1 ppm (1 C, CH-CH-N-CH-CH).

### 2.3. Preparation of kaolinite and nanohybrid materials

Well crystallized kaolinite (KGa-1b, Georgia) was obtained from the Source Clays Repository of the Clay Minerals Society (Purdue University, West Lafayette, Indiana, USA). Purification of KGa-1b and intercalation of dimethylsulfoxide (DMSO) to obtain the K-DMSO pre-intercalate were achieved by following previously described procedures (Letaief and Detellier, 2009; Tonle et al., 2009; Tunney and Detellier, 1993; Tunney and Detellier, 1997). For the grafting of HEPC, 0.5 g of K-DMSO was dispersed in 2 g of ionic liquid. The mixture was stirred under nitrogen for 4 h, the temperature being gradually increased to 180 °C. The resulting mixture was fully washed three times with isopropanol to remove the excess of ionic liquids and dried in an oven at 80 °C for 5 h. Each material was then stirred for 48 h in 100 mL of distilled water to remove the ungrafted compounds which were trapped in the interlayer space. The grafted kaolinite (K-HEPC) was recovered by centrifugation and dried in an oven at 70 °C for 5 h.

### 2.4. Characterization

Powder XRD patterns were recorded using a Philips PW 3710 diffractometer operating with Cu-K $\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) using a generator with a voltage of 45 kV and a current of 40 mA.

Thermal gravimetric analyses (TGA) were recorded using a TA instrument Q5000 under nitrogen flow (100 mL/min) at a heating rate of 10 °C/min.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra in solution were recorded using a Bruker 400 MHz spectrometer. Solid-state  $^{13}\text{C}$  NMR CP/MAS spectrum was collected on a Bruker AVANCE 200 spectrometer spinning at 4500 Hz.

KBr pellets were prepared for the IR analysis and the spectrum recorded on the ThermoScientific Nicolet 6700 FT-IR equipment.

For electrochemical characterization, thin film electrodes were prepared. Kaolinite or K-HEPC was coated on the surface of a glassy carbon electrode (GCE). 5  $\mu\text{L}$  of a suspension of a mixture of clay and carboxymethylcellulose (4 and 0.5 g L<sup>-1</sup> respectively) was carefully deposited on GCE and dried in open air for about 45 min. The thin film electrode was used as a working electrode, a platinum plate as a counter electrode and an Ag/AgCl (KCl saturated) electrode as a reference. All the potential values in this work are referred to this reference electrode. Cyclic voltammetry was used for all electrochemical experimentations using a VersaSTAT 3 potentiostat controlled by V3-studio software. Before the recording of the signal, a pre-concentration step at open circuit was performed during which the modified electrode was immersed in SA or GA solutions; the electrode was then removed, rinsed with distilled water, transferred to the detection medium consisting of the electrochemical cell containing a 0.1 M phosphate buffer solution (PBS) pH 7 and the signal immediately recorded.

### 2.5. Adsorption and desorption experiments

In a series of vials containing 6 mg of K-HEPC, 3 mL of a solution of SA or GA at varying concentrations was introduced. The vials were sealed and agitated for 5 h. The contents were then centrifuged and the residual concentration in the supernatant determined by UV spectroscopy at 296 nm and 260 nm for SA and GA respectively. For desorption experiments, intercalated composites (K-HEPC/SA and K-HEPC/GA) were prepared by dispersing 100 mg of nanohybrid kaolinite in 50 mL of SA or GA 0.05 M solution. After centrifugation, the solids were washed

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